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PHYSICAL-CHEMICAL TREATMENT OF MUNICIPAL WASTES BY RECYCLED MAGNESIUM CARBONATE

A. P. Black, et al

Gainesville

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27 Abstract
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PHYSICAL-CHEMICAL TREATMENT OF MUNICIPAL WASTES BY RECYCLED MAGNESIUM CARBONATE

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ABSTRACT

The applicability to municipal wastes of the recently discovered magnesium carbonate-lime water treatment process has been investigated. A sixteen-month laboratory study was conducted and was followed by an eight-month pilot plant study. Four wastewaters with COD values varying from 200 to 1,500 mg/ℓ were examined. Bench-scale coagulation studies designed to compare the effect of added $MgCO_3$ with treatment by lime only showed a 0%-30% greater reduction in effluent COD residuals. Color and turbidity reduction by the magnesium-plus-lime process averaged 50%-85% greater when compared to treatment by lime only. A series of 72-hour pilot plant runs was conducted with the magnesium precipitated increased after each three-day period. Effluent characteristics improved as the amount of magnesium precipitated was increased. Influent and filter effluent samples were collected every four hours and analyzed for COD, TOC, total phosphorus, alkalinity, hardness, calcium, and magnesium. Values for BOD were determined from composited samples. The percentage reduction in chemical (COD) and biological (BOD) oxygen-consuming substances ranged from a low of 70% for no magnesium ion precipitated to a high of 90% for 30 milligrams per liter of magnesium ion precipitated. Higher dosages have not yet been investigaged.

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SECTION I. CONCLUSIONS

The treatment of municipal wastewaters by coagulation with recycled magnesium bicarbonate and lime has been investigated. Due to the present unabailability of magnesium carbonate tri-hydrate, magnesium sulfate was used as the source of "make-up" magnesium. The magnesium hydroxide formed by its precipitation with the magnesium naturally present in the waste was converted by carbonation of the sludge to the highly soluble bicarbonate and recycled.

The wastewaters studied may be grouped with respect to their total COD values into three categories.

a. Wastes containing less than 400 mg/ℓ of total COD.

b. Wastes containing from 400-800 mg/ℓ total COD.

c. Wastes containing more than 800 mg/ℓ total COD.

1. The data showed from 10% to 30% more *total* COD removed from category (b) and (c) wastes by coagulation with recycled magnesium bicarbonate and lime than could be obtained by treatment with lime only. This level of reduction was also achieved for both BOD and TOC. Jar tests indicate that even greater percentage removals of total COD should result from the coagulation of very high COD wastes, that is, in the range 1,200-2,000, but pilot plant runs in this range have not as yet been made.

2. Values for total phosphorus in the clear, settled effluent from the coagulation unit were normally less than 0.1 ppm P except when sludge carryover took place. As reported by Menar and Jenkins (53) and verified in this research, any phosphate solids that escape the sedimentation basin (pH 11.5) will be resolubilized in the carbonation basin (pH 9.5). Filtration following carbonation is of no value in removing phosphate.

3. Values for both suspended solids and color were very much lower than when lime alone was used. Vaues for suspended solids before carbonation were usually less than 2 ppm and residual color after stabilization was usually less than 5 pcu.

4. Coagulation of the low total COD waste of category (a) with recycled magnesium and lime resulted in small but measurable

improvement over values when lime alone was used. This is probably due to the fact that the percentage of soluble COD, less likely to be removed by coagulation than COD due to suspended solids, is normally highest in wastes having low total COD values. However, the much greater percentage reductions in phosphate, suspended solids and color found for category (b) and (c) wastes were also found for category (a).

5. Although, as noted above, the greatest percentage reduction in total COD was found where suspended solids were high, usually in the range of 175-250 mg/ℓ, the soluble COD values of the wastes of categories (b) and (c) were reduced by 60%-70%. Values for soluble BOD and TOC were reduced by about 40%. This reduction was brought about by precipitating at least 20 mg/ℓ of magnesium ion.

6. In the operation of the pilot plant, rapid mixing was not used. Best results were obtained by adding the recycled magnesium bicarbonate liquor to the raw waste effluent at the splitter box and the lime at the influent to the upflow flocculator. A rotational speed of 2 rpm was found sufficient for adequate mixing and the formation of large, heavy flocs, their density greatly increased by the presence of the coprecipitated calcium carbonate. The flocculator performed as a fluidized bed, retaining the occasional larger particles.

7. The addition of about 4 ppm of activated silica or 0.10 ppm of a strongly anionic high molecular weight polymer such as A23 increased floc size and density and improved settling.

8. Due to the high buffer capacity of the coagulated wastewater in the high pH range employed, it was found that more accurate control of the treatment process could be obtained by differential titration than by determining the pH value. Hydroxide alkalinity in the range 140-180 mg/ℓ (corresponding roughly to the pH range 11.4-11.6) was found to produce the lowest values for residual COD.

SECTION II. RECOMMENDATIONS

The municipal wastewater of the city of Gainesville, Florida, is typically a weak-medium strength wastewater as defined by the COD test. A very light industrial load is presently imparted to the sewage. One of the main advantages of the magnesium process demonstrated in the laboratory is the superior treatment of high-strength wastewaters over lime alone. This fact needs to be evaluated on a pilot plant scale by adding high strength wastes to the raw sewage. Industrial wastes or digestor supernatant would serve as supplements.

While many chemical coagulants are available, lime coagulation was the only one used for comparison during this study. Further laboratory and pilot plant studies need to be performed utilizing higher dosages of magnesium carbonate and lime to completely evaluate the magnesium process.

The sewages studied had a ratio of insoluble to soluble COD (and BOD) of three to one. Wastewaters which have a low insoluble and high soluble COD (BOD) need to be evaluated in both jar tests and the pilot plant in order to determine the effect of the magnesium coagulation on dissolved constituents.

Phosphorus and heavy metals are removed by the coagulation process and, therefore, are contained in the sludge. The reclaimed magnesium and calcium values need to be evaluated to determine the presence or absence of phosphates and heavy metals. A specific problem is the rate of phosphorus accumulation in the calcium carbonate prior to recalcination. The possibility of separation of the phosphate fraction by flotation requires evaluation.

The amounts of organic and ammonium nitrogen and heavy metals removed by the lime magnesium process should be determined and compared with removals obtained with other coagulants.

SECTION III. INTRODUCTION

Over the last few years it has become apparent that conventional "secondary" biological sewage treatment processes do not provide the degree of treatment required for effective water pollution control. Well-operated biological treatment processes can provide at best approximately 90% removal of suspended solids and biochemical oxygen demand with little or no reduction in nitrogen and phosphorus levels. This level of performance will not meet the increasingly stringent demands for better water quality and more effective pollution control. As a result, considerable effort is now being devoted to the development of physicochemical processes capable of accomplishing the degree of treatment required by more exacting effluent standards (1,2). The traditional approach to the application of physicochemical processes to wastewater treatment has centered on providing "tertiary" treatment for wastes which have already undergone conventional "secondary" biological treatment. This increment of tertiary level physicochemical treatment to conventional biological processes results in significant additional treatment cost. In addition, the effective operation of a tertiary treatment system depends on consistent and effective operation of the biological secondary process. Because of these factors the effort is now being made to develop successful physicochemical treatment processes which can be applied to municipal primary wastes (3).

Review of Literature

The first attemps to chemically treat sewage were made in Paris in 1740 (4). In the next 100 years chemical treatment processes became well established in England. Most of these plants used iron and lime salts as coagulants. The promotion of several such processes was done on the basis of the supposed value of the sludge as fertilizer. The chemical processes gradually lost favor because they were expensive, did not produce a stabilized effluent, and yielded larger quantities of sludge. By 1910 most of them had been discarded in favor of plain settling followed by biological processes. Chemical treatment never generated much interest in the United States during this period.

In 1929, Rudolphs *et al.* (5) revived interest in chemical treatment by describing the increased settling rates of sewage solids brought about by the addition of small doses of ferric chloride. The most widespread use of chemical treatment was in improving the degree of treatment achieved by sedimentation. Many combinations of chemicals were tried (1,6-9).

Between 1936 and 1941, Rudolfs and Gehm published a series of papers dealing with coagulation of sewage (10-17). They found the optimum pH ranges for coagulation with iron salts to be 2.5 to 3.5 and 9.5 to 10.5 with some slight shifting of the optimum pH caused by variations in septicity, quantity and type of industrial wastes present and quantity of iron coagulant used.

In England a number of attempts were made to improve the quality of effluent from chemical treatment of sewage.

The Laughlin process (18) consisted of adding ferric chloride, lime, and paper pulp to raw sewage, settling for 1 hour and then filtering. Suspended solids removals of 85% to 95% and BOD removals of 65% to 85% were obtained. Results comparable to those achieved by the Laughlin process were achieved at Great Neck, N.Y., by passing coagulated and settled sewage through two vacuum filters, using paper pulp as a filter medium (19).

The Guggenheim process consisted of the screening of raw sewage, coagulation with lime and ferric sulfate, flocculation, sedimentation, and zeolite filtration (20). A final effluent with 1 mg per liter suspended solids, 5 mg per liter BOD, and 2 to 3 mgs per liter total nitrogen was produced.

A scheme was also proposed using the Aero-Accelerator manufactured by Infilco (21). Calcium carbonate sludge from a water softening plant was added to raw sewage suspended solids in a 1:1 ratio. Ninety-five percent BOD reduction was obtained.

The Landreth process consists of coagulating raw sewage with lime and then subjecting the sewage and lime floc to electrolysis in a basin containing iron electrodes (4).

Ferric chloride was used as the coagulant in the Stevenson process (22,23). Recovery and reuse of the coagulant was attempted.

Alum recovery was practiced in Holland, and about 80% recovery was achieved (20). The work done at Lake Tahoe has shown that an acid alum recovery scheme is only feasible if the chemical coagulation is not designed to remove phosphates (24). Lime recovery by recalcination was conducted at the sewage treatment plant at Syracuse University (25). This study indicates that coagulant recovery can be achieved by recalcination.

Activated silica has also been used in sewage treatment. Hurwitz and Williamson (26) used copperas and silica for chemical sewage treatment. Rudolfs (27) also did some preliminary work using acid activated silica.

Studies have been made on the use of proteins as coagulant aids (28). Compounds of gelatin and ferric chloride ("Ferrigel") and of gelatin and aluminum chloride were found to be effective coagulants.

Background Information

Until 1957, a recalcination of sludge produced by softening high magnesium waters by the lime soda process was considered impossible. Wide adoption of recalcination had been retarded by the fact that no successful method for the physical separation of the calcium carbonate from the other components had been developed. In that year, Black and Eidsness (29) developed a process to selectively dissolve the magnesium hydroxide from the calcium carbonate using carbon dioxide gas. This gas would be readily available from the lime kiln.

At Dayton, Ohio, which softens well waters high in magnesium, a high quality quicklime has been produced using this process since 1958. The supernatant from this process, containing the magnesium which had been converted to the soluble bicarbonate form is then discharged to the river.

In 1968 the necessity of meeting new and rigorous standards for such waste discharges required another method of disposal. This impetus led to the discovery of a relatively simple and inexpensive method of recovering the magnesium as a carbonate. In this process, which was developed by A. P. Black (30), all wastewater is recovered and recycled. The only waste material, when present, is clay, which may easily be landfilled.

Briefly, the process employed at Dayton is as follows. Sludge produced from the softening operation is pumped to a sludge recarbonation basin where it is mixed with scrubbed kiln gas containing about 20% CO_2. The magnesium hydroxide is dissolved from the calcium carbonate. This slurry then passes to a thickener from which the clear supernatant containing the magnesium, now in the form of soluble magnesium bicarbonate, will overflow and be passed to a heat exchange unit where it will be warmed to 40°C. The solution will then flow to an aeration basin equipped with mechanical stirrers. Precipitation of the magnesium carbonate as the trihydrate is rapid and essentially complete in 90 minutes. The snow-white product will then be vacuum filtered, dried and bagged for shipment. The thickener sludge is sent to a kiln and calcined to a high quality quicklime. For every 1 ton of lime fed, 1.3 tons to 1.4 tons are recovered. The excess is derived from the calcium carbonate in the raw water. In turbid waters, the sludge consists of $CaCO_3$, $Mg(OH)_2$, and clay. The $Mg(OH)_2$ is dissolved and recovered as described above. The clay is separated from the $CaCO_3$ by flotation and the purified $CaCO_3$ calcined.

Calculations made on the basis of data supplied by a major midwestern municipal softening plant treating 75 MGD of hard, turbid water indicate a saving in chemical costs of approximately $340,000 a year. This saving results from:

1. Elimination of alum.

2. Reduction in cost of lime due to recalcining.

3. The use of kiln stack gas both for carbonation of sludge and finished water pH adjustment.

Not included in this figure were the profits from the sale of excess magnesium carbonate and excess lime and the reduction in demand for chlorine used for disinfection. Elimination of prechlorination and reduced postchlorination are possible since bacterial disinfection and virus inactivation occur at the process operating pH of above 11. Certain intangible benefits would accrue such as prevention of precipitation of alum in the distribution system and the advantage of producing and stocking your own chemicals for treatment in event of strikes and national emergencies.

During 1970, coagulation studies were carried out at the University of Florida's Environmental Engineering Laboratory by Black and Thompson (31,32) comparing magnesium carbonate and alum as coagulants for organic color and turbidity removal. Water from approximately 20 major cities along with several synthetic solutions were evaluated utilizing the jar test procedure. These waters represented a wide range in physical and chemical characteristics. In summation, the following conclusions were reached:

1. Magnesium carbonate is superior to alum for the removal of both turbidity and color.

2. The flocs formed are larger, heavier, and settle faster than the alum flocs. Therefore, the capacity of the plants will increase.

3. Color is much more significant than turbidity in determining the necessary chemical dosages.

4. Release of the coagulated color during the sludge carbonation step is not a problem when the color of the water is less than 150.

5. The use of magnesium carbonate produces a treated water with superior physical and chemical characteristics compared to alum treated waters.

Waters high in magnesium can be treated at a much lower cost then waters low in magnesium since no make up in magnesium is required and a lower coagulating pH is possible.

Scope of Investigation

The purpose of this investigation is to evaluate the feasibility of treating domestic sewage and industrial wastes with magnesium carbonate hydrolyzed by lime. This process appears attractive for several reasons. First, a new water treatment process using magnesium carbonate hydrolyzed by lime as the coagulating agent has been developed in which the magnesium carbonate is recycled (31,32). For hard waters the process will lead to a surplus of magnesium carbonate. This excess could be used for chemical treatment of sewage. In addition, the use of magnesium carbonate hydrolyzed by lime has the potential of removing a greater quantity of COD, BOD and phosphorus than lime alone for sewage treatment. Bench scale tests will be designed to determine the magnitude of this potential. The possibility of removing ammonia nitrogen by this process will also be investigated. Recovery and recycling of the magnesium and lime from the sludge will be a primary consideration. If the results are encouraging, a pilot plant will be constructed.

SECTION IV. METAL AMMONIUM PHOSPHATES

Nutrients in wastewaters are important because, upon discharge to a water course, they promote biological responses that interfere with the desired uses of water by man.

Over the last few years it has become apparent that conventional secondary biological treatment processes do not provide the degree of treatment required for effective water pollution control. Secondary biological processes do not reduce the total level of nutrients, but merely convert them from one form to another. Moreover, when digestor supernatant liquor is recycled within the plant, a two- or three-fold increase in the total nutrients being discharged occurs.

The addition of tertiary chemical treatment for removal of nutrients has thus become necessary. An estimate of the relative costs of the different stages of waste treatment has been reported (1) as follows:

Primary treatment	3¢ to 5¢/1,000 gallons
Secondary treatment	8¢ to 11¢/1,000 gallons
Tertiary treatment to remove nutrients	17¢ to 23¢/1,000 gallons
Total	28¢ to 39¢/1,000 gallons

Unfortunately, the use of chemicals has been a constant consuming process with no prospect of recovery and reuse. In addition, the sludges produced by these tertiary processes constitute a difficult waste disposal problem in themselves. Therefore, only a few plants have provided such treatment.

Recently, a new water treatment process using magnesium carbonate hydrolyzed by lime as the coagulating agent has been developed in which the magnesium carbonate is recycled and reused (31,32). Its effectiveness as a coagulant and the savings to be achieved by recycling both the lime and the $MgCO_3$ dictate that studies should be carried out to determine its effectiveness for treatment of municipal and industrial wastes and mixtures of the two.

While phosphate may be removed by a number of different processes, the removal of ammonia nitrogen is much more difficult. One attractive possibility would be its removal with phosphate as a metal ammonium phosphate, the best-known compound of this type being magnesium ammonium phosphate, $MgNH_4PO_4 \cdot 6H_2O$. A gravimetric method for the accurate determination of either magnesium or of phosphate by precipitation as the double phosphate has been employed for many years and its solubility under the conditions of its precipitation is less than 1 milligram per liter (33).

Literature Survey

An extensive literature search was conducted regarding the preparation and properties of the compound, magnesium ammonium phosphate. Theoretically, the compound reaches its minium solubility at pH 10.7 (34). A number of investigators have reported solubility data for magnesium ammonium phosphate, but a comparison of the various data reveals a lack of agreement among the published results (35-38).

Bridger (35)	180 mg/ℓ
Bube (36)	170 mg/ℓ
Szekeres (37)	160 mg/ℓ
Uncles (38)	140 mg/ℓ

All solubility data were based on phosphate analyses except that of Uncles and Smith, which were based on magnesium analysis. The rounded average of the values reported is 160 mg/ℓ. Expressed as phosphorus (P) the solubility is 20 mg/ℓ, as magnesium (Mg) the solubility is 16 mg/ℓ, and as ammonia (NH_3) the solubility is 11 mg/ℓ, or as ammonia nitrogen (NH_3-N) 9 mg/ℓ.

The solubility in the range of values listed would preclude its precipitation from either untreated municipal wastewater or from trickling filter effluent unless special conditions resembling those used in analytical procedures are employed. The use of excess Mg^{++} ion and pH variations appeared to be the only variables worthy of study and they were investigated.

Background Data

In the initial studies using the municipal waste treatment plant of the City of Gainesville, Florida, the chemical and biological treatment processes were constantly monitored. The two processes (activated sludge and trickling filter) are operated in parallel and treat approximately the same total volume. The influent to the trickling filter plant is by gravity flow while the activated sludge plant influent is from force mains and lift stations. During the course of this research, the digestor supernatant liquor was alternately recycled to each of the processes on a four-month basis. The reasons for this procedure were:

1. The loss of a prime location for disposal of a considerable volume of digestor supernatant liquor.

2. The desirability to investigate the increased nutrient concentration that would result from in-plant recycling of digestor supernatant liquor.

3. To evaluate the physical, chemical, and biological problems that would prevail as a result of recycling the digestor supernatant liquor.

Data from three different recycling situations were compiled. The first situation (before October 11, 1971) was prior to losing a prime disposal site and, consequently, only half of the total digestor supernatant liquor was recycled to the activated sludge process (Table 1). The second situation (before February 18, 1972) was brought about by the loss of this disposal site for digestor supernatant liquor, and resulted in a total volume of 30,000 gallons of digestor supernatant liquor being recycled to the primary clarifiers of the trickling filter process (Table 2). Case three (after February 18, 1972) consisted of the total flow from the digestor being recycled to the activated sludge process (Table 3).

The majority of jar tests for nutrient removal as a metal ammonium phosphate were carried out under situation two.

Analytical Methods

The methods for analyses conducted on the wastewater streams were in accordance with *Standard Methods for the Examination of Water and Wastewater* (33), *Methods for Chemical Analysis of Water and Wastes* (39), and "Methods for Analyses of Selected Metals in Water by Atomic Absorption" (40).

All nutrient analyses were performed using the Technicon AutoAnalyzer.* Initial comparisons between ammonia nitrogen concentrations obtained by distillation and titration with the Technicon phenate method were widely divergent. However, upon addition of the catalyst, sodium nitroprusside, the phenate method (39) yielded values which checked with those obtained by the distillation procedure (33). Phosphate analyses were performed using the single reagent method (41). Total phosphate was determined by treating samples with a strong acid solution and ammonium perfulfate, and subsequently heating in an autoclave for 30 minutes at 121°C (15-20 psi).

Magnesium and calcium were determined titrimetrically (33) and by atomic absorption (40). The atomic absorption unit was utilized in

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*Technicon, Tarrytown, N.Y.

Table 1

Average Characteristics of Effluents
(Digestor Supernatant Returned to Plant #2)
Prior to October 11, 1971

	Plant #1 Trickling Filter Plant Secondary Clarifier Effluent	Plant #2 Contact Stabilization Plant Secondary Clarifier Effluent	Digestor Supernatant
pH	7.1	7.1	7.0
Turbidity	18	15	--
COD	81	62	--
BOD	46	28	--
NH_3-N as N	8.7	7.2	600
Ortho-PO_4 as P	4.3	3.8	100
Alkalinity	104	84	2,800
Hardness	97	90	700

Table 2

Average Characteristics of Effluents
(Digestor Supernatant Returned to Plant #1)
October 11, 1971, to February 18, 1972

	Plant #1 Trickling Filter Plant Secondary Clarifier Effluent	Plant #2 Contact Stabilization Plant Secondary Clarifier Effluent	Digestor Supernatant
pH	7.2	7.1	--
Turbidity	30	18	--
COD	115	75	--
BOD	35	20	--
NH_3-N	25	8	560
Ortho-PO_4, as P	9	4	80
Alkalinity	150	115	3,200
Hardness	110	105	750

Table 3

Average Characteristics of Effluents (Digestor Supernatant Returned to Plant #2) After February 18, 1972

	Plant #1 Trickling Filter Plant Secondary Clarifier Effluent	Plant #2 Contact Stabilization Plant Secondary Clarifier Effluent	Digestor Supernatant
pH	7.2	7.2	—
Turbidity	22	20	—
COD	108	83	—
BOD	40	33	—
NH_3-N	15	16	580
Ortho-PO_4 as P	6	8	72
Alkalinity	130	120	--
Hardness	100	100	--

combination with a DBG grating spectrophotometer and potentiometric recorder with scale expander.*

Prior to analysis for total alkalinity, total hardness, calcium, magnesium, nitrogen, phosphorus, chemical oxygen demand, and biochemical oxygen demand, all chemically treated wastewater samples were filtered through Whatman No. 2 paper.

Magnesium Ammonium Phosphate

In the initial phase of the jar tests, wastewater analyses showed a surplus of ammonia nitrogen over phosphorus on the order of 2 to 1. Therefore, phosphate had to be added to the wastewater in order to achieve the proper N/P ratio for precipitation of magnesium ammonium phosphate. The calculations to assure the proper proportions are as follows:

$$NH_3\text{-}N = 1 \qquad P = \frac{30.97}{14} = 2.2 \times NH_3\text{-}N$$

$$NH_3\text{-}N = 1 \qquad PO_4 = \frac{94.97}{14} = 6.8 \times NH_3\text{-}N$$

$$NH_3\text{-}N = 1 \qquad Mg = \frac{24.3}{14} = 1.7 \times NH_3\text{-}N$$

$$NH_3\text{-}N = 1 \qquad MgCO_3\cdot 3H_2O = \frac{138.4}{14} = 9.9 \times NH_3\text{-}N$$

The phosphorus was added as potassium dihydrogen phosphate (1 mℓ = 10 mg P).

All jar tests were conducted using an improved version of the multiple stirrer.† All pH measurements were made using a pH meter with a combination glass and Ag/AgCl electrode.** The pH meter was calibrated daily.

The first jar test was conducted on August 12, 1971 (Table 4). The alkalinity of the waste was significantly higher than the total

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*Beckman Model 1301, Beckman Instruments, Inc., Fullerton, California.

†Coffman Ind., Inc., Kansas City, Kansas.

**Corning Model 7, Corning Glass Works, Philadelphia, Pennsylvania.

Table 4

Initial Test for N and P Removal

JAR. NO.	DOSAGE IN mg/l			pH	Turbidity	ALK		STAB TO pH	ALK		HARDNESS			Ca.	Mg.	BOD	COD	NH_3 N	TP	Ortho PO_4	
	P	$MgCO_3$ $3H_2O$	Lime			OH	CO_3		CO_3	HCO_3	C	NC	T	as $CaCO_3$	as $CaCO_3$						
1	10	80	225	10.3														9.0		0.20	
2	12	90	235	10.5														9.0		0.14	
3	14	100	245	10.7														9.0		0.10	
4	16	110	255	10.9														9.5		0.08	
5	18	120	265	11.0														9.5		0.04	
6	20	130	275	11.1												20	40	10.5		0.04	

CHARACTERISTICS OF RAW WASTEWATER	
ALKALINITY AS $CaCO_3$	137
TOTAL HARDNESS AS $CaCO_3$	96
CALCIUM AS $CaCO_3$	51
MAGNESIUM AS $CaCO_3$	45
TOTAL COD	86
SOLUBLE COD	
TOTAL TOC	
SOLUBLE TOC	
TOTAL BOD	44
SOLUBLE BOD	
NH_3 - N	11.2
O-PO_4	7.4

Comments: Secondary Effluent Trickling Filter Plant
Rapid Mix for 10 minutes @ 100 RPM
Slow Mix for 20 minutes @ 30 RPM
Settled for 30 minutes
Filtered samples through Whatman #2 prior to COD, N, and P analysis

Floc large, significant amount of floc settled during slow mix.
Supernatant clear.

COD% Removal - 58
P% Removal - 99
N% Removal - 8
BOD% Removal - 54

hardness, representing a situation of "negative" noncarbonate hardness. This is typical of domestic wastes and required higher lime dosages than were anticipated. The data indicated that more phosphorus was removed as pH was increased, but that less ammonia nitrogen was removed. Theoretically, the compound, magnesium ammonium phosphate, reaches its minimum solubility at pH 10.7 (34). This test demonstrated an increase in ammonia nitrogen once this pH value was exceeded. Approximately 60% of the COD and 54% of the BOD were removed by coagulation with magnesium carbonate and lime.

The second and third jar tests (Tables 5 and 6) were designed to study the lime demand of this wastewater to achieve a desired pH level. Simultaneously, a study of the ability of lime to remove phosphorus was carried out. Phosphorus removal, of course, increased with increasing pH values.

These tests were then repeated using only added $MgCO_3$ and phosphate (Table 7). The magnesium dosage was extended to include a three to one excess of magnesium. No significant removals of ammonia nitrogen were observed. Phosphorus removal increased with increasing pH values.

Table 8 shows jar tests performed to precipitate magnesium ammonium phosphate in the pH range of 9.2 to 9.7. Although ammonia nitrogen was not removed, phosphorus was precipitated as pH increased.

As mentioned previously and shown in Table 1, the ammonia nitrogen concentration in the secondary wastewater is less than the minimum ammonia nitrogen value as magnesium ammonium phosphate. Therefore, these tests apparently show that removal of ammonia nitrogen is not possible in this concentration range.

Other Metal Ammonium Phosphates

The preliminary findings suggested a further literature search aimed at exposing other metal ammonium phosphates with lower solubilities (35).

Copper ammonium phosphate, solubility 9 mg/ℓ, would produce an ammonia nitrogen concentration of less than 1 mg/ℓ. A jar test was conducted in order to precipitate this compound (Table 9). The failure to produce significant nitrogen removal and the cost of $CuSO_4$ precluded further consideration of this compound.

Iron ammonium phosphate, solubility 95 mg/ℓ, and manganese ammonium phosphate, solubility 38 mg/ℓ, were two other possible compounds for consideration. However, the cost, lack of recycling probability, and high nitrogen solubility eliminated these compounds.

Table 5

Coagulation - Flocculation of Trickling Filter Effluent with Lime in pH Range 7.9-9.6

JAR. NO.	DOSAGE IN mg/l			pH		ALK		STAB TO pH	ALK		HARDNESS			Ca.	Mg.	Ortho PO_4					
	P		Lime			OH	CO_3		CO_3	HCO_3	C	NC	T	as $CaCO_3$	as $CaCO_3$						
1	20		30	7.9					0	146			115	94	21	10					
2	20		60	8.5					22	108			95	74	21	10					
3	20		90	8.9					54	78			80	57	23	5.6					
4	20		100	9.2					82	53			80	60	20	3.7					
5	20		110	9.4					100	40			88	60	28	2.9					
6	20		125	9.6					118	31			92	65	27	1.6					

CHARACTERISTICS OF RAW WASTEWATER

ALKALINITY AS $CaCO_3$ 115
TOTAL HARDNESS AS $CaCO_3$ 91
CALCIUM AS $CaCO_3$ . . . 55
MAGNESIUM AS $CaCO_3$ . . 36
TOTAL COD . . . .
SOLUBLE COD . . . . . .
TOTAL TOC . . . .
SOLUBLE TOC . . . . . .
TOTAL BOD . . . .
SOLUBLE BOD . . . . . .
NH_3 - N 9.5
O-PO_4 . . . . 14.7

Table 6

Coagulation - Flocculation of Trickling Filter Effluent with Lime in pH Range 10.0-11.6

JAR. NO.	DOSAGE IN mg/l			pH		ALK		STAB TO pH	ALK		HARDNESS			Ca.	Mg.	Ortho PO_4					
	P.		Lime			OH	CO_3		CO_3	HCO_3	C	NC	T	as $CaCO_3$	as $CaCO_3$						
1	20		150	10.0		0	152						105	87	18	1.0					
2	20		200	10.5		49	98						100	87	13	0.7					
3	20		250	10.9		79	76						105	102	3	0.6					
4	20		300	11.2		130	54						135	134	1	0.3					
5	20		350	11.4		179	56						186	185	1	0.2					
6	20		400	11.6		226	54						225	225	0	0.2					

CHARACTERISTICS OF RAW WASTEWATER

ALKALINITY AS $CaCO_3$ 102
TOTAL HARDNESS AS $CaCO_3$ 94
CALCIUM AS $CaCO_3$ . . . 55
MAGNESIUM AS $CaCO_3$ . . 39
TOTAL COD . . . . . .
SOLUBLE COD . . . . . .
TOTAL TOC . . . . . .
SOLUBLE TOC . . . . . .
TOTAL BOD . . . . . .
SOLUBLE BOD . . . . . .
NH_3-N 8.7
O-PO_4 . . . . 4.1

Gravity Flow Raw Sewage NO_3-N 0.09 mg/l

Trickling Filter Plant Effluent NO_3-N 1.12 mg/l

Table 7

Nutrient Removal Utilizing Magnesium and Phosphorus

JAR. NO.	DOSAGE IN mg/l			pH		ALK		STAB TO pH	ALK		HARDNESS			Ca.	Mg.	NH_3 N	Ortho PO_4				
	P	$MgCO_3 \cdot 3H_2O$				OH	CO_3		CO_3	HCO_3	C	NC	T	as $CaCO_3$	as $CaCO_3$						
1	20	50		7.5												7.58	20.0				
2	20	100		7.8												7.58	17.0				
3	20	150		8.4												7.50	15.0				
4	20	200		8.8												7.58	11.0				
5	20	250		9.0												7.58	11.0				
6	20	300		9.1												7.52	10.0				

CHARACTERISTICS OF RAW WASTEWATER

ALKALINITY AS $CaCO_3$ 102
TOTAL HARDNESS AS $CaCO_3$ 94
CALCIUM AS $CaCO_3$ . . . 55
MAGNESIUM AS $CaCO_3$ . . 39
TOTAL COD . . . .
SOLUBLE COD . . . . . .
TOTAL TOC . . . . . .
SOLUBLE TOC . . . . . .
TOTAL BOD . . . . . .
SOLUBLE BOD . . . . . .
NH_3-N 8.10
O-PO_4 . . . . 4.51

Comments: Trickling Filter Effluent
Pinpoint floc in all 6
Poor Settling
Samples filtered through Whatman #2
prior to nutrient analysis

Total P - 7.03

Table 8

Nutrient Removal as Magnesium Ammonium Phosphate

JAR. NO.	DOSAGE IN mg/l			pH		ALK		STAB TO pH	ALK		HARDNESS			Ca.	Mg.	NH_3 N	Ortho PO_4				
	P	$MgCO_3$	Lime			OH	CO_3		CO_3	HCO_3	C	NC	T	as $CaCO_3$	as $CaCO_3$						
1	20	80	50	9.2												7.52	20				
2	20	100	60	9.3												7.52	20				
3	20	120	70	9.4												7.17	14				
4	20	140	80	9.5												7.43	10				
5	20	160	90	9.6												7.25	9				
6	20	180	100	9.7												7.17	6				

CHARACTERISTICS OF RAW WASTEWATER

ALKALINITY AS $CaCO_3$ 108

TOTAL HARDNESS AS $CaCO_3$ 96

CALCIUM AS $CaCO_3$ . . . 56

MAGNESIUM AS $CaCO_3$ . . 40

TOTAL COD . . . .

SOLUBLE COD . . . . . .

TOTAL TOC . . . .

SOLUBLE TOC . . . . . .

TOTAL BOD . . . .

SOLUBLE BOD . . . . . .

NH_3 - N 8.12

O-PO_4 . . . . 4.80

Comments: Trickling Filter Effluent
Rapid Mix 15 minutes @ 100 RPM
Slow Mix 30 minutes @ 30 RPM
All samples filtered prior to
nutrient analyses

Supernatant cloudy
Fair settling

Table 9

Nutrient Removal as Copper Ammonium Phosphate

JAR. NO.	DOSAGE IN mg/l			pH		ALK		STAB TO pH	ALK		HARDNESS			Ca.	Mg.	NH_3 N					
	P	$CuSO_4$				OH	CO_3		CO_3	HCO_3	C	NC	T	as $CaCO_3$	as $CaCO_3$						
1	10	60		6.7				8.8								4.5					
2	12	80		6.0				8.2								5.1					
3	14	100		5.5				7.9								5.3					
4	16	120		5.0				7.8								6.2					
5	18	140		4.5				7.6								6.2					
6	20	160		4.0				7.4								6.2					

CHARACTERISTICS OF RAW WASTEWATER

ALKALINITY AS $CaCO_3$ 112
TOTAL HARDNESS AS $CaCO_3$ 98
CALCIUM AS $CaCO_3$ . . . 53
MAGNESIUM AS $CaCO_3$ . . 45
TOTAL COD . . . . . .
SOLUBLE COD . . . . . .
TOTAL TOC . . . .
SOLUBLE TOC . . . . . .
TOTAL BOD . . . .
SOLUBLE BOD . . . . . .
NH_3-N 7.6
O-PO_4 . . . . 3.8

Comments: Trickling Filter Effluent
100 RPM for 20 minutes
30 RPM for 30 minutes

Poor floc and settling

Calcium Ammonium Phosphates

According to Lange (42) calcium ammonium phosphate, $CaNH_4PO_4 \cdot H_2O$, is insoluble. Lehr *et al.* (43,44) have prepared several different fertilizers containing this compound.

A series of jar tests were conducted over a one-week period similar to those shown in Tables 5 and 6. Twenty-four jars were dosed with the same amount of phosphorus and slightly increasing lime dosages. The entire pH range from 9.2 to 11.5 was covered with the pH of each jar increased by only one-tenth of a pH unit. Tables 10 through 13 show no significant ammonia nitrogen removal. Primary effluent to the trickling filter beds was used as the wastewater source during these jar tests.

Tennessee Valley Authority (45) has described the properties of over 200 fertilizers as well as the methods of preparation. The calcium ammonium phosphates described in this publication by TVA were prepared by adjusting the pH prior to introduction of the calcium compound. Up to this point in this research, lime had been used to adjust the pH value in the jars.

Tables 14 and 15 are examples of jar tests conducted by adjusting the pH with trisodium phosphate and disodium hydrogen phosphate prior to adding a calcium compound. These tests were performed in an effort to prepare the compound $CaNH_4PO_4 \cdot H_2O$. The experiments were not successful. Efforts were then made to prepare the compound $Ca(NH_4)_2(HPO_4)_2 \cdot H_2O$, dimorph A, at very low pH values. Tables 16 and 17 show the data obtained. An elevated temperature was utilized to avoid interference from the more soluble dimorph B. The lack of evidence for nutrient removal suggested examination of the pure salts and evaluations of nutrient removal from synthetic solutions.

The next approach employed was to use solutions of ammonium chloride in distilled water. The concentrations of ammonium ion were 10 mg/ℓ and 20 mg/ℓ, respectively. Tables 18 and 19 depict the jar tests conducted in an effort to precipitate the ammonium as $CaNH_4PO_4 \cdot H_2O$. Two solutions were also prepared from tap water and ammonium chloride. The concentrations of ammonium ion were 10 mg/ℓ and 20 mg/ℓ, respectively. Tables 20 and 21 show the jar tests performed in an effort to precipitate the ammonium as $CaNH_4PO_4 \cdot H_2O$. The ammonium content of the distilled water samples and the tap water samples was reduced by 0% to 30% and 0% to 10%, respectively. This reduction has been found in several series of jar tests and is probably due to adsorption of ammonia by floc particles.

Reference samples of $CaNH_4PO_4 \cdot H_2O$ and $Ca(NH_4)_2(HPO_4)_2 \cdot H_2O$, dimorph A, were obtained* for solubility measurements. Lehr† cautioned

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*Tennessee Valley Authority, Division of Chemical Development, Muscle Shoals, Alabama.

†J. R. Lehr, personal communication.

Table 10

Nutrient Removal as Calcium Ammonium Phosphate

JAR. NO.	DOSAGE IN mg/l			pH		ALK		STAB TO pH	ALK		HARDNESS			Ca.	Mg.	NH_3 N					
		Lime				OH	CO_3		CO_3	HCO_3	C	NC	T	as $CaCO_3$	as $CaCO_3$						
1		100		9.2												10.0					
2		105		9.3												10.0					
3		110		9.4												9.0					
4		115		9.5												9.0					
5		120		9.6												9.0					
6		125		9.7												9.5					

CHARACTERISTICS OF RAW WASTEWATER

ALKALINITY AS $CaCO_3$ 110

TOTAL HARDNESS AS $CaCO_3$ 96

CALCIUM AS $CaCO_3$ . . . . ______

MAGNESIUM AS $CaCO_3$ . . ______

TOTAL COD . . . . ______

SOLUBLE COD . . . . . . ______

TOTAL TOC . . . . ______

SOLUBLE TOC . . . . . . ______

TOTAL BOD . . . . ______

SOLUBLE BOD . . . . . . ______

NH_3-N 12.4

O-PO_4 . . . . 7.2

Comments: Primary Effluent - Trickling Filter
Fast Mix 100 RPM for 10 minutes
Slow Mix 20 RPM for 20 minutes
Samples filtered - Whatman #2 before nutrient analysis

Table 11

Nutrient Removal as Calcium Ammonium Phosphate

JAR. NO.	DOSAGE IN mg/l			pH		ALK		STAB TO pH	ALK		HARDNESS			Ca	Mg.	NH_3 N					
		Lime				OH	CO_3		CO_3	HCO_3	C	NC	T	as $CaCO_3$	as $CaCO_3$						
7		140		9.8												9.5					
8		145		9.9												9.5					
9		150		10.0												9.0					
10		155		10.1												9.0					
11		160		10.2												9.0					
12		170		10.3												9.0					

CHARACTERISTICS OF RAW WASTEWATER

ALKALINITY AS $CaCO_3$ 112

TOTAL HARDNESS AS $CaCO_3$ 94

CALCIUM AS $CaCO_3$ . . . ______

MAGNESIUM AS $CaCO_3$ . . ______

TOTAL COD . . . . . . ______

SOLUBLE COD . . . . . ______

TOTAL TOC . . . . . . ______

SOLUBLE TOC . . . . . ______

TOTAL BOD . . . . . . ______

SOLUBLE BOD . . . . . ______

NH_3 - N 11.6

O-PO_4 . . . . 6.3

Comments: Primary Effluent - Trickling Filter
Fast Mix 100 RPM for 10 minutes
Slow Mix 20 RPM for 20 minutes
Samples filtered - Whatman #2 before nutrient analysis

Table 12

Nutrient Removal as Calcium Ammonium Phosphate

JAR NO.	DOSAGE IN mg/l			pH		ALK		STAB TO pH	ALK		HARDNESS			Ca.	Mg.	NH_3 N					
		Lime				OH	CO_3		CO_3	HCO_3	C	NC	T	as $CaCO_3$	as $CaCO_3$						
13		190		10.4												9.0					
14		210		10.5												9.0					
15		220		10.6												9.0					
16		230		10.7												9.0					
17		240		10.8												9.0					
18		250		10.9												9.0					

CHARACTERISTICS OF RAW WASTEWATER

ALKALINITY AS $CaCO_3$ 108
TOTAL HARDNESS AS $CaCO_3$ 94
CALCIUM AS $CaCO_3$ . . . ______
MAGNESIUM AS $CaCO_3$ . . ______
TOTAL COD . . . . . . ______
SOLUBLE COD . . . . . . ______
TOTAL TOC . . . . . . ______
SOLUBLE TOC . . . . . . ______
TOTAL BOD . . . . . . ______
SOLUBLE BOD . . . . . . ______
NH_3-N 12.2
O-PO_4 . . . . 6.5

Comments: Primary Effluent - Trickling Filter
Fast Mix 100 RPM for 10 minutes
Slow Mix 20 RPM for 20 minutes
Samples filtered - Whatman #2 before nutrient analysis

Table 13

Nutrient Removal as Calcium Ammonium Phosphate

JAR NO.	DOSAGE IN mg/l			pH		ALK		STAB TO pH	ALK		HARDNESS			Ca.	Mg.	NH_3 N					
		Lime				OH	CO_3		CO_3	HCO_3	C	NC	T	as $CaCO_3$	as $CaCO_3$						
19		260		11.0												8.5					
20		280		11.1												8.5					
21		300		11.2												8.5					
22		325		11.3												8.5					
23		350		11.4												9.0					
24		370		11.5												9.0					

CHARACTERISTICS OF RAW WASTEWATER

ALKALINITY AS $CaCO_3$ 110

TOTAL HARDNESS AS $CaCO_3$ 95

CALCIUM AS $CaCO_3$ . . . ______

MAGNESIUM AS $CaCO_3$ . . ______

TOTAL COD . . . . . . ______

SOLUBLE COD . . . . . ______

TOTAL TOC . . . . . . ______

SOLUBLE TOC . . . . . ______

TOTAL BOD . . . . . . ______

SOLUBLE BOD . . . . . ______

NH_3 - N 11.8

O-PO_4 . . . . . 6.5

Comments: Primary Effluent - Trickling Filter
Fast Mix 100 RPM for 10 minutes
Slow Mix 20 RPM for 20 minutes
Samples filtered - Whatman #2 before nutrient analysis

Table 14

Nutrient Removal as $CaNH_4PO_4 \cdot H_2O$

JAR. NO.	DOSAGE IN mg/l			pH		ALK		STAB TO pH	ALK		HARDNESS			Ca.	Mg.	NH_3 N					
	P	pH	Lime			OH	CO_3		CO_3	HCO_3	C	NC	T	as $CaCO_3$	as $CaCO_3$						
1	50	8.1	40	8.5												21					
2	50	8.1	50	8.7												21					
3	50	8.1	60	8.9												20					
4	50	8.1	70	9.1												20					
5	50	8.1	90	9.5												20					
6	50	8.1	110	9.7												20					

CHARACTERISTICS OF RAW WASTEWATER

ALKALINITY AS $CaCO_3$ ____
TOTAL HARDNESS AS $CaCO_3$ ____
CALCIUM AS $CaCO_3$ . . . ____
MAGNESIUM AS $CaCO_3$ . . ____
TOTAL COD . . . . . . ____
SOLUBLE COD . . . . . ____
TOTAL TOC . . . . . . ____
SOLUBLE TOC . . . . . ____
TOTAL BOD . . . . . . ____
SOLUBLE BOD . . . . . ____
NH_3-N 23
O-PO_4 8

Comments: Rapid Mix - 100 RPM - 15 minutes
Slow Mix - 30 RPM - 10 minutes
Secondary Effluent
Trickling Filter Plant

P added as Na_2HPO_4

Table 15

Nutrient Removal as $CaNH_4PO_4 \cdot H_2O$

JAR. NO.	DOSAGE IN mg/l			pH		ALK		STAB TO pH	ALK		HARDNESS			Ca.	Mg.	NH_3 N					
	P	pH	$CaCl_2$			OH	CO_3		CO_3	HCO_3	C	NC	T	as $CaCO_3$	as $CaCO_3$						
1	50	10.0	0	10.0												21					
2	50	10.0	100	9.7												20					
3	50	10.0	150	9.4												20					
4	50	10.0	200	9.1												20					
5	50	10.0	250	8.8												20					
6	50	10.0	300	8.5												17					

CHARACTERISTICS OF RAW WASTEWATER

ALKALINITY AS $CaCO_3$ ____________
TOTAL HARDNESS AS $CaCO_3$ ____________
CALCIUM AS $CaCO_3$ . . . ____________
MAGNESIUM AS $CaCO_3$ . . ____________
TOTAL COD . . . . . . ____________
SOLUBLE COD . . . . . ____________
TOTAL TOC . . . . . . ____________
SOLUBLE TOC . . . . . ____________
TOTAL BOD . . . . . . ____________
SOLUBLE BOD . . . . . ____________
NH_3 - N 21
O-PO_4 6

Comments: Rapid Mix 100 RPM for 20 minutes
Slow Mix 20 RPM for 40 minutes
Secondary Effluent
Trickling Filter Plant

Padded as Na_3PO_4

Table 16

Nutrient Removal as $Ca(NH_4)_2(HPO_4)_2 \cdot H_2O$

JAR. NO.	DOSAGE IN mg/l			pH		ALK		STAB TO pH	ALK		HARDNESS			Ca.	Mg.	NH_3 N					
	P	$CaCO_3$				OH	CO_3		CO_3	HCO_3	C	NC	T	as $CaCO_3$	as $CaCO_3$						
1	60	150		5.8												27					
2	60	180		5.8												27					
3	60	210		5.8												27					
4	60	240		5.8												27					
5	60	270		5.8												27					
6	60	300		5.8												27					

CHARACTERISTICS OF RAW WASTEWATER

ALKALINITY AS $CaCO_3$ ________

TOTAL HARDNESS AS $CaCO_3$ ________

CALCIUM AS $CaCO_3$ . . . ________

MAGNESIUM AS $CaCO_3$ . . ________

TOTAL COD . . . . . . ________

SOLUBLE COD . . . . . ________

TOTAL TOC . . . . . . ________

SOLUBLE TOC . . . . . ________

TOTAL BOD . . . . . . ________

SOLUBLE BOD . . . . . ________

NH_3-N 27

O-PO_4 9

Comments: Jars held in water bath at 50°C
pH adjusted to 5.8 by H_2SO_4
Rapid Mix 100 RPM for 15 minutes
Slow Mix 30 RPM for 10 minutes
Secondary Effluent
Trickling Filter Plant

Padded as NaH_2PO_4

Table 17

Nutrient Removal as $Ca(NH_4)_2(HPO_4)_2 \cdot H_2O$

JAR. NO.	DOSAGE IN mg/l			pH		ALK		STAB TO pH	ALK		HARDNESS			Ca.	Mg.	NH_3 N					
	P	Lime				OH	CO_3		CO_3	HCO_3	C	NC	T	as $CaCO_3$	as $CaCO_3$						
1	60	60		5.8												25					
2	60	70		5.8												25					
3	60	80		5.8												25					
4	60	90		5.8												25					
5	60	100		5.8												25					
6	60	110		5.8												25					

CHARACTERISTICS OF RAW WASTEWATER

ALKALINITY AS $CaCO_3$ ____________

TOTAL HARDNESS AS $CaCO_3$ ____________

CALCIUM AS $CaCO_3$ . . . ____________

MAGNESIUM AS $CaCO_3$ . . ____________

TOTAL COD . . . . . . ____________

SOLUBLE COD . . . . . ____________

TOTAL TOC . . . . . . ____________

SOLUBLE TOC . . . . . ____________

TOTAL BOD . . . . . . ____________

SOLUBLE BOD . . . . . ____________

NH_3-N 25

O-PO_4 . . . . ____________

Comments: pH adjusted to 5.8 by H_2SO_4
Water bath temperature 56°C
Rapid Mix - 100 RPM - 10 minutes
Slow Mix - 30 RPM - 5 minutes
Secondary Effluent
Trickling Filter Plant

Padded as NaH_2PO_4

Table 18

Nutrient Removal as Calcium Ammonium Phosphate

JAR. NO.	DOSAGE IN mg/l			pH		ALK		STAB TO pH	ALK		HARDNESS			Ca.	Mg.	NH_3 N					
	P.	Lime				OH	CO_3		CO_3	HCO_3	C	NC	T	as $CaCO_3$	as $CaCO_3$						
1	165	20		9.2												10.3					
2	165	30		9.5												7.7					
3	165	35		9.7												7.7					
4	165	40		9.9												8.3					
5	165	45		10.1												9.0					
	165	50		10.4												9.0					

CHARACTERISTICS OF RAW WASTEWATER

ALKALINITY AS $CaCO_3$ ______
TOTAL HARDNESS AS $CaCO_3$ ______
CALCIUM AS $CaCO_3$ . . . ______
MAGNESIUM AS $CaCO_3$ . . ______
TOTAL COD . . . . . . ______
SOLUBLE COD . . . . . ______
TOTAL TOC . . . . . . ______
SOLUBLE TOC . . . . . ______
TOTAL BOD . . . . . . ______
SOLUBLE BOD . . . . . ______
NH_3-N 10.3
O-PO_4 . . . . ______

Comments: Distilled Water and Ammonium Chloride
Padded as Na_2HPO_4

Table 19

Nutrient Removal as Calcium Ammonium Phosphate

JAR NO.	DOSAGE IN mg/l			pH		ALK		STAB TO pH	ALK		HARDNESS			Ca.	Mg.	NH_3 N					
	P	$CaSO_4$				OH	CO_3		CO_3	HCO_3	C	NC	T	as $CaCO_3$	as $CaCO_3$						
1	330	300		9.0												20.0					
2	330	300		9.2												17.0					
3	330	300		9.4												17.0					
4	330	300		9.6												16.5					
5	330	300		9.8												16.5					
6	330	300		10.0												15.0					

CHARACTERISTICS OF RAW WASTEWATER

ALKALINITY AS $CaCO_3$ ____
TOTAL HARDNESS AS $CaCO_3$ ____
CALCIUM AS $CaCO_3$ . . . ____
MAGNESIUM AS $CaCO_3$ . . ____
TOTAL COD . . . . . . ____
SOLUBLE COD . . . . . ____
TOTAL TOC . . . . . . ____
SOLUBLE TOC . . . . . ____
TOTAL BOD . . . . . . ____
SOLUBLE BOD . . . . . ____
NH_3 - N 20
O-PO_4 . . . . ____

Comments: Distilled Water and Ammonium Chloride
Calcium in two-fold excess
NaOH used to adjust pH

P added as Na_2HPO_4

Table 20

Nutrient Removal as Calcium Ammonium Phosphate

JAR. NO.	DOSAGE IN mg/l			pH		ALK		STAB TO pH	ALK		HARDNESS			Ca.	Mg.	NH_3 N					
	P	Lime				OH	CO_3		CO_3	HCO_3	C	NC	T	as $CaCO_3$	as $CaCO_3$						
1	165	10		9.5												9.0					
2	165	13		9.8												9.0					
3	165	16		10.0												9.0					
4	165	20		10.3												8.3					
5	165	25		10.7												9.0					
6	165	30		11.0												9.0					

CHARACTERISTICS OF RAW WASTEWATER

ALKALINITY AS $CaCO_3$ ______

TOTAL HARDNESS AS $CaCO_3$ ______

CALCIUM AS $CaCO_3$ . . . 68

MAGNESIUM AS $CaCO_3$ . . ______

TOTAL COD . . . . . . ______

SOLUBLE COD . . . . . ______

TOTAL TOC . . . . . . ______

SOLUBLE TOC . . . . . ______

TOTAL BOD . . . . . . ______

SOLUBLE BOD . . . . . ______

NH_3-N 9.7

O-PO_4 . . . . ______

Comments: Tap Water and Ammonium Chloride

Padded as Na_2HPO_4

Table 21

Nutrient Removal as Calcium Ammonium Phosphate

JAR. NO.	DOSAGE IN mg/l			pH		ALK		STAB TO pH	ALK		HARDNESS			Ca.	Mg.	NH_3 N					
		P				OH	CO_3		CO_3	HCO_3	C	NC	T	as $CaCO_3$	as $CaCO_3$						
1		160		9.0																	
2		160		9.2												20.0					
3		160		9.4												18.5					
4		160		9.6												18.5					
5		160		9.8												18.5					
6		160		10.0												20.2					

CHARACTERISTICS OF RAW WASTEWATER

ALKALINITY AS $CaCO_3$ ____
TOTAL HARDNESS AS $CaCO_3$ ____
CALCIUM AS $CaCO_3$ . . . ____
MAGNESIUM AS $CaCO_3$ . . ____
TOTAL COD . . . . . . ____
SOLUBLE COD . . . . . ____
TOTAL TOC . . . . . . ____
SOLUBLE TOC . . . . . ____
TOTAL BOD . . . . . . ____
SOLUBLE BOD . . . . . ____
NH_3 - N 20.1
O-PO_4 . . . . ____

Comments: Tap Water and Ammonium Chloride
pH adjusted by NaOH
P added as $CaHPO_4$

that the solubility data obtained for $CaNH_4PO_4 \cdot H_2O$ might not be equilibrium values, the reason being that the solution produced by the incongruent dissolution process shifts progressively in composition toward the mono- or di-ammonium phosphate fields (44). As this shift occurs, new solid phases can appear in the following sequence: apatite, octacalcium phosphate, dicalcium phosphate dihydrate, and finally $Ca(NH_4)_2(HPO_4)_2 \cdot H_2O$. Once apatite forms, it tends to persist as a metastable solid phase, thereby preventing solubility measurements of $CaNH_4PO_4 \cdot H_2O$ under true equilibrium conditions.

Table 22 shows the analytical results obtained by adding various amounts of $CaNH_4PO_4 \cdot H_2O$ to distilled water and intermittently stirring over several time periods. A specific ion electrode was used for these ammonia determinations.* The high ammonia content of these solutions preclude further consideration as a means for nutrient removal.

Table 22

Solubility of Calcium Ammonium Phosphate
(Distilled Water at 22°C)

Parameters	mg/ℓ	mg/ℓ	mg/ℓ	mg/ℓ
$CaNH_4PO_4 \cdot H_2O$	500[a]	500[b]	5,000[a]	5,000[b]
Calcium	12	5	12	5
Phosphate	90	60	900	600
Ammonia	18	22	150	170

[a] Stirred for 2 minutes.

[b] Stirred for 120 minutes.

The removal of both ammonia and phosphate in a one-step process based on the formation of an insoluble metal ammonium phosphate was not found to be feasible. While these compounds can be quantitavely precipitated under laboratory conditions, their solubilities are too large to meet effluent standards for municipal waste treatment.

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*Orion, Inc., Cambridge, Massachusetts.

SECTION V. COAGULATION OF SEWAGES

Upon finalizing the metal ammonium phosphate production phase, the main emphasis of work turned to the evaluation of other parameters in the coagulation of sewage. Initially, secondary effluent was selected to be used. However, after a few jar tests, three problem areas were readily apparent. These were:

1. The removal efficiencies for BOD and COD were on the order of 55% to 65%.
2. The production of a highly buffered system by the biological treatment process complicates the coagulation procedure.
3. The most vexacious problem in sewage treatment (production, treatment, and disposal of biological sludges) would not be eliminated. This would be true since the coagulation step was being utilized as a tertiary treatment step.

In addition, the costs of adding another step in sewage treatment must increase the overall cost regardless of the process. Faced with these formidable objections, the decision was made to examine the magnesium carbonate-lime process as the primary treatment step. Consequently, samples of the raw sewage after comminution were subjected to coagulation.

Jar Tests

The collection of background data on the Gainesville raw sewage showed a wide variation in alkalinity (Table 23). Thus, the amount of lime required for treatment would correspond to these variations. Corroberation of this type and level of fluctuation was received from sewage plants in Orlando and Ft. Lauderdale. Initial jar tests (Tables 24-26) proved highly successful. The BOD and COD analyses were performed on the wastewater after coagulation and filtration through Whatman No. 2 filter paper. Although carbonation was carred out, BOD and COD analyses did not include this step. Additional removals are possible from the carbonation step as shown in Table 32b. Table 27 shows the first Total Organic Carbon* (TOC) analyses conducted. All analyses were conducted before carbonation, although normally a treatment plant will include this step. Phosphorus removal was extremely efficient (99%), and the residual is less than

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*Beckman Total Carbon Analyzer.

Table 23

Total Alkalinity Fluctuations (24-Hour Composite)

Date	Time	Alkalinity	Date	Time	Alkalinity
3-14-72	10 A.M.	190	3-15-72	12 P.M.	132
	11 A.M.	206		1 A.M.	130
	12 M.	194		2 A.M.	90
	1 P.M.	188		3 A.M.	104
	2 P.M.	188		4 A.M.	102
	3 P.M.	184		5 A.M.	102
	4 P.M.	180		6 A.M.	110
	5 P.M.	178		7 A.M.	120
	6 P.M.	146		8 A.M.	230
	7 P.M.	148		9 A.M.	206
	8 P.M.	136			
	9 P.M.	132			
	10 P.M.	132			
	11 P.M.	132			

Note: Total alkalinity - 154
Total hardness - 100
Calcium as $CaCO_3$ - 58
Magnesium as $CaCO_3$ - 42
pH - 7.5

Table 24

Coagulation of Raw Sewage*

JAR. NO.	DOSAGE IN mg/l			pH		ALK		STAB TO pH	ALK		HARDNESS			Ca.	Mg.	BOD	COD				
	$MgCO_3$	Lime				OH	CO_3		CO_3	HCO_3	C	NC	T	as $CaCO_3$	as $CaCO_3$						
1	50	265		11.3		77	88	9.0	24	88			84	66	18						
2	60	270		11.3		78	96	9.0	24	98			90	62	28						
3	70	275		11.3		78	94	8.7	12	120			100	80	20						
4	80	280		11.3		78	96	8.8	16	106			88	60	28	21	61				
5	80	280		11.3		78	100	8.8	16	104			82	56	26	19	53				
6	90	285		11.3		76	108	8.8	16	126			106	82	24	21	55				

*17-hour composite

CHARACTERISTICS OF RAW WASTEWATER

ALKALINITY AS $CaCO_3$ 130
TOTAL HARDNESS AS $CaCO_3$ 96
CALCIUM AS $CaCO_3$ . . . 52
MAGNESIUM AS $CaCO_3$ . . 44
TOTAL COD 316
SOLUBLE COD . . . . . .
TOTAL TOC . . . .
SOLUBLE TOC . . . . . .
TOTAL BOD 105
SOLUBLE BOD . . . . . .
NH_3-N . . . .
O-PO_4 . . . .

Comments: COD and BOD analyses prior to carbonation
pH after $MgCO_3 \cdot 3H_2O$ added - 8.5
#4, 5, 6 - settle best
All clear after 10 minutes settling

Table 25

Coagulation of Raw Sewage*

JAR. NO.	DOSAGE IN mg/l			pH		ALK		STAB TO pH	ALK		HARDNESS			Ca.	Mg.	COD					
	$MgCO_3$	Lime				OH	CO_3		CO_3	HCO_3	C	NC	T	as $CaCO_3$	as $CaCO_3$						
1	40	260		11.0		36	54	9.0	40	100			86	54	32	85					
2	60	270		11.1		38	52	9.0	40	100			82	78	4	78					
3	70	290		11.2		39	50	9.0	44	86			72	72	0	76					

*24-hour composite

CHARACTERISTICS OF RAW WASTEWATER

ALKALINITY AS $CaCO_3$	154
TOTAL HARDNESS AS $CaCO_3$	100
CALCIUM AS $CaCO_3$	58
MAGNESIUM AS $CaCO_3$	42
TOTAL COD	410
SOLUBLE COD	
TOTAL TOC	
SOLUBLE TOC	
TOTAL BOD	
SOLUBLE BOD	
NH_3-N	
O-PO_4	

Comments: pH after $MgCO_3$ - 8.6
COD analyses before carbonation
Excellent floc
Good settling in 10 minutes

Table 26

Coagulation of Raw Sewage*

JAR. NO.	DOSAGE IN mg/l			pH	Turbidity	ALK		STAB TO pH	ALK		HARDNESS			Ca.	Mg.	BOD	COD				
	$MgCO_3$	Lime				OH	CO_3		CO_3	HCO_3	C	NC	T	as $CaCO_3$	as $CaCO_3$						
1	40	275		11.2	9	88	92									45	76				
2	60	287		11.2	6	90	100						140	110	30	40	73				
3	100	307		11.2	5	82	108									35	73				

*24-hour composite

CHARACTERISTICS OF RAW WASTEWATER

ALKALINITY AS $CaCO_3$	148
TOTAL HARDNESS AS $CaCO_3$	94
CALCIUM AS $CaCO_3$ . . .	54
MAGNESIUM AS $CaCO_3$ . .	40
TOTAL COD	380
SOLUBLE COD	
TOTAL TOC	
SOLUBLE TOC	
TOTAL BOD	145
SOLUBLE BOD	
NH_3 - N	
O-PO_4	

Comments: Carbonation not conducted

Turbidity values high due to 1-hour time lapse before sampling. Allows for formation of $CaCO_3$

Excellent flocs
Supernatant bright

Table 27

Coagulation of Raw Sewage*

JAR. NO.	DOSAGE IN mg/l			pH		ALK		STAB TO pH	ALK		HARDNESS			Ca.	Mg.	BOD	COD	NH_3	TOC	Ortho P	
	$MgCO_3$	Lime				OH	CO_3		CO_3	HCO_3	C	NC	T	as $CaCO_3$	as $CaCO_3$						
1	100	200		11.0		60	228						224	140	84		58		35		
2	100	215		11.1		74	220						220	140	80		58		32		
3	100	225		11.2		90	200						200	124	76		57		34		
4	100	250		11.3		96	192						160	104	56		56		30		
5	100	275		11.4		128	136						134	102	32	19	54	9	29	.02	
6	100	300		11.5		140	140						132	106	26		54		31		

*8:30 AM grab sample

CHARACTERISTICS OF RAW WASTEWATER

ALKALINITY AS $CaCO_3$ 160

TOTAL HARDNESS AS $CaCO_3$ 95

CALCIUM AS $CaCO_3$ . . . 55

MAGNESIUM AS $CaCO_3$ . . 40

TOTAL COD 387

SOLUBLE COD . . . . . . ______

TOTAL TOC 132

SOLUBLE TOC . . . . . ______

TOTAL BOD 136

SOLUBLE BOD . . . . . ______

NH_3 - N 12

O-PO_4 . . . . 4.5

Comments: Sample #6 stabilized to pH 9.0 with CO_2
Total alkalinity - 104
Total hardness - 50
Flocs excellent
Good settling

'Mg ppt. (as $CaCO_3$)

Jar 1 - 28
2 - 32
3 - 36
4 - 56
5 - 80
6 - 86

any level yet reported in the literature (Table 28). Other parameters are shown for comparative purposes. An even higher removal efficiency is assured since adsorption by granular activated carbon would be part of this treatment process.

Table 28

Chemical Treatment of Raw Sewage

Authors	Treatment Method		Residuals Effluent Quality (mg/ℓ)				
			COD	BOD	TOC	NH_3	P
Villiers (46)	Lime	Before	187	78	79	—	9.2*
	Clarification[a]	After	84	39	36	—	0.3
Weber (47)	Ferric	Before	—	65	70	35	80*
	Chloride[b]	After	—	15	30	20^{+}	<5
Smith (48)	Lime[c]	Before	420	100	—	—	6**
		After	125	20	—	—	0.7
Smith (48)	Lime +	Before	420	100	—	—	6**
	Ferric Floc[d]	After	92	20	—	—	0.7
Hannah (49)	Lime[e]	Before	265	139	78	—	10*
		After	66	28	23	—	0.4
Bishop (50)	Lime +	Before	347	142	118	—	8.7*
	Ferric Iron[f]	After	66	31	26	—	0.3
This Research	$MgCO_3 \cdot 3H_2O$	Before	387	136	134	33	4.5**
	+ Lime[g]	After	54	19	29	22	0.02

[a] Dosage - 150-300 mg/ℓ (lime form not reported).
[b] Dosage - 200-350 mg/ℓ.
[c] Dosage - 150 and 300 mg/ℓ (lime as $Ca(OH)_2$).
[d] Dosage - 100 and 175 mg/ℓ (lime as $Ca(OH)_2$).
[e] Dosage - 350-400 mg/ℓ (lime as CaO).
[f] Dosage - 350 mg/ℓ and 5 mg/ℓ (lime as CaO).
[g] Dosage - 100 and 275 mg/ℓ ($MgCO_3 \cdot 3H_2O$ and 98% $Ca(OH)_2$).

*Total P.
**Ortho P.

Drum Tests

Table 29 shows the results of the first drum test. The wastewater was not carbonated to pH 9.0 prior to analyses for BOD and COD. The purpose of this drum test was to recover $MgCO_3 \cdot 3H_2O$ from the sludge produced. A recovery of 97% was obtained.

Clinoptilolite

Clinoptilolite is a natural exchange material selective for the ammonium ion. This material was used on bench scale tests by Sullivan (51) at the University of Florida. Ammonia residuals from feedwaters containing 2 to 5 mg/ℓ NH_3-N averaged 0.12 to 0.32 mg/ℓ NH_3-N.

Mercer (52) further studied this compound on a laboratory and pilot plant scale. Laboratory tests showed 99% removal, while pilot plant studies produced 97% removal (16 mg/ℓ to 1.5 mg/ℓ) at 6 gpm/sq ft flow rate.

Lime is the regenerant for the ammonia saturated clinoptilolite. The volume of liquid waste from the regeneration step is small and, of course, high in ammonia. This waste liquid was air stripped by Mercer, but low efficiency was observed for ammonia removal.

If succesful, this process would be adaptable to the Gainesville project, since

1. Lime is recovered and recycled in the normal process, and a portion of this lime could be used for regeneration.

2. The concentrated ammonia waste stream could be treated with sulfuric acid to produce ammonium sulfate, a valuable fertilizer.

Table 30 shows the initial ammonia removal test using the exchange material.* The analyses were performed using the Orion specific ion electrode.†

Benefit of the Magnesium Ion

Numerous jar and drum tests designed to study the several variables involved in the coagulation, flocculation, and settling of the untreated raw waste of the City of Gainesville have been presented. The data have indicated but have not clearly proved

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*W. R. Grace Co., Clarkesville, Maryland

†Orion, Inc., Cambridge, Massachusetts.

Table 29

Coagulation of Raw Sewage. Drum Test

JAR. NO.	DOSAGE IN mg/l			pH		ALK		STAB TO pH	ALK		HARDNESS			Ca.	Mg.	BOD	COD				
	$MgCO_3$	Lime				OH	CO_3		CO_3	HCO_3	C	NC	T	as $CaCO_3$	as $CaCO_3$						
1	74	250		11.3		92	76						146	120	26	25	46				
2	74	265		11.4		100	72						140	130	10	25	41				
3	74	280		11.5		108	64						140	130	10	25	38				

CHARACTERISTICS OF RAW WASTEWATER

ALKALINITY AS $CaCO_3$	108
TOTAL HARDNESS AS $CaCO_3$	90
CALCIUM AS $CaCO_3$	50
MAGNESIUM AS $CaCO_3$	40
TOTAL COD	188
SOLUBLE COD	
TOTAL TOC	
SOLUBLE TOC	
TOTAL BOD	125
SOLUBLE BOD	
NH_3-N	
$O-PO_4$	

Comments: Grab sample at 4:00 AM. 97% $MgCO_3 \cdot 3H_2O$ recovery. Three 55-gallon drums of raw sewage were coagulated with $MgCO_3 \cdot 3H_2O$ and $Ca(OH)_2$ using the optimum dosages as determined by the jar test procedures. This quantity of sewage provided sufficient sludge for the accurate determination of magnesium recovery. The clear supernatant was decanted. The sludge from the three drums was composited and carbonated to pH 7.5. The sludge was filtered and the volume of filtrate and its alkalinity determined. The percentage recovery was obtained from the alkalinity, the magnesium present in the raw sewage, and the magnesium added as coagulant.

Table 30

Ammonia Removal

Source	mg/ℓ as NH_3^+
Raw sewage	12
Coagulated and filtered sewage	9
After clinoptilolite	<0.6

that the addition of $MgCO_3$ as a recycled coagulant provides settled effluents superior to those where lime alone is used, and superior to the effluents produced by other investigators employing lime alone. However, most waters contain some magnesium which may or may not have precipitated during the work of others and which may have influenced the data obtained. It was decided, therefore, to begin a series of jar tests designed to definitely establish, if possible, the fact that the addition of recycled $MgCO_3$ is capable of producing results superior to those produced with lime alone. The problem was to secure a municipal wastewater low in magnesium since both the untreated Gainesville and University of Florida wastewaters contain from 28-48 ppm magnesium expressed as $CaCO_3$. Untreated municipal wastes were shipped to Gainesville from North Miami and Montgomery, Alabama. Waste from North Miami contained almost as much Mg as Gainesville waste, but that from Montgomery, which has a very soft river water as its source of water, contained only 8-12 ppm magnesium as $CaCO_3$ or 1-3 ppm as Mg^{++}.

Gainesville, Florida, Sewage

Table 31 presents the data obtained from an exploratory jar test in which increasing dosages of lime only were added to jars 1-3 and the same dosages of lime plus 80 ppm $MgCO_3$ were added to jars 4-6. Increasing lime dosages showed higher removal efficiencies. The same lime dosages when combined with the magnesium ion removed less COD until a hydroxide alkalinity of 140 mg/ℓ was reached. At this point, the lowest COD residual of all jars tested was observed. Of course, one must realize that the wastewater being tested naturally contains about 8 mg/ℓ magnesium ion. Upon observing this action, a series of tests was designed to show the effectiveness of increasing the magnesium ion while maintaining a hydroxide alkalinity of 140 mg/ℓ. Table 32a demonstrates the observed results. The first two jars were set up to determine the effect of lime alone at this hydroxide alkalinity and also to show the reproducibility of our testing method.

Table 31

Gainesville Waste Water COD Removal by Lime and $MgCO_3 \cdot 3H_2O$ Plus Lime

JAR. NO.	DOSAGE IN mg/l			pH		ALK		STAB TO pH	ALK		HARDNESS			Ca.	Mg.	COD					
	$MgCO_3$	Lime				OH	CO_3		CO_3	HCO_3	C	NC	T	as $CaCO_3$	as $CaCO_3$						
1	--	100		11.0					180	40						76					
2	--	200		11.2		70	160									73					
3	--	300		11.6		180	80									65					
4	80	100		10.9		0	280									86					
5	80	200		11.1		70	200									82					
6	80	300		11.5		140	100									61					

CHARACTERISTICS OF RAW WASTEWATER

ALKALINITY AS $CaCO_3$ 166
TOTAL HARDNESS AS $CaCO_3$
CALCIUM AS $CaCO_3$ . . .
MAGNESIUM AS $CaCO_3$ . .
TOTAL COD 490
SOLUBLE COD . . . . .
TOTAL TOC . . . . . .
SOLUBLE TOC . . . . .
TOTAL BOD . . . . . .
SOLUBLE BOD . . . . .
NH_3 - N . . . .
O-PO_4 . . . .

Table 32a

Effect of Increasing $MgCO_3 \cdot 3H_2O$ and Lime on Removal of COD, TOC, and Total Phosphorus

JAR. NO.	DOSAGE IN mg/l			pH		ALK		STAB TO pH	ALK		HARDNESS			Ca.	Mg.	COD	TOC	T.P.			
	$MgCO_3$	Lime				OH	CO_3		CO_3	HCO_3	C	NC	T	as $CaCO_3$	as $CaCO_3$						
1	0	295		11.3		138	116						150	123	27	79	41	.60			
2	0	295		11.3		138	120						150	123	27	76	38	.44			
3	25	325		11.4		136	128						158	133	25	74	35	.16			
4	50	350		11.4		142	116						150	128	22	69	33	.12			
5	75	375		11.4		160	100						154	138	16	68	35	.10			
6	100	400		11.4		172	96						158	143	15	65	33	.09			

CHARACTERISTICS OF RAW WASTEWATER

ALKALINITY AS $CaCO_3$ ______ 224
TOTAL HARDNESS AS $CaCO_3$ ______ 108
CALCIUM AS $CaCO_3$ . . . ______ 75
MAGNESIUM AS $CaCO_3$ . . ______ 33
TOTAL COD . . . . . . ______ 490
SOLUBLE COD . . . . . ______
TOTAL TOC . . . . . . ______ 156
SOLUBLE TOC . . . . . ______
TOTAL BOD . . . . . . ______
SOLUBLE BOD . . . . . ______
NH_3-N . . . . ______
O-PO_4 . . . . ______

Comments: Progressively larger and heavier flocs
Marked difference between jars 3 and 4
Progressively better settling and clarity
See Table 32b for effect of carbonation

Jar No.	Mg^{++} pptd (as $CaCO_3$)
1	6
2	6
3	25
4	46
5	69
6	88

The results showed generally good agreement. The last four jars were designed to maintain a constant pH while increasing the magnesium ion. Lime had to be increased also in order to maintain a constant pH and precipitate the additional magnesium ion. A measurable increase of COD removed occurred with increasing magnesium precipitation. At the same time, samples for TOC and total P were collected and sent to a private laboratory for analyses. The results still show significantly lower residuals for total P and better removal efficiencies for TOC when compared to other methods (Table 28).

Another point of interest has been whether carbonation would effect a further reduction in the parameters under consideration. Table 32b shows the results obtained by carbonating the supernatant from the previous jar test (Table 32a). While no significant decrease in TOC or total P occurred, a measurable reduction in COD did take place in all jars. The TOC and total P results were provided by a private laboratory. The total hardness was reduced from 180 mg/ℓ to 52 mg/ℓ in the highest magnesium dosed jar.

Table 33 shows the effect of increasing pH on COD removal for lime alone and magnesium plus lime. A significantly lower COD residual was obtained using magnesium plus lime at all comparative pH values. In addition, when comparing lime alone at pH 11.5 with magnesium plus lime at pH 11.4, a much better COD removal is observed at the lower pH value. Thus, magnesium does contribute to higher removal efficiencies as judged by COD reduction.

Tables 34-37 show four series of jar tests designed to evaluate the mg/ℓ of COD removed per mg of magnesium. Two Gainesville wastewaters were examined: (1) a COD of 374 mg/ℓ , and (2) a COD of 520 mg/ℓ. Samples were run in duplicate from pH 11.1—11.6 for each 0.1 change in pH. The COD removal/mg of magnesium precipitated was different for each set of duplicate jars. However, if the 12 jars in each series are averaged, the removal of COD/mg of magnesium for the 374 mg/ℓ COD waste is 17.6 mg/ℓ COD removed/mg/ℓ magnesium precipitated and for the 520 mg/ℓ waste the removal is 20.1 mg/ℓ COD removed/mg/ℓ of magnesium precipitated. The total magnesium ion present in each jar (present naturally plus added) was almost the same, namely, 28.8 mg/ℓ magnesium for the 374 mg/ℓ COD and 29.8 mg/ℓ for the 520 mg/ℓ COD.

Table 38 was designed to investigate the reductions in values for soluble, insoluble and total COD, BOD, and TOC values by use of combinations of $MgCO_3$ and lime.

The data indicate that the dosages of $MgCO_3 \cdot 3H_2O$ added differed too little to significantly affect the parameters investigated. The slight improvement was, however, proportional to Mg precipitated.

The stabilized and filtered effluents were passed through granular carbon and ion exchange columns, with the same dramatic

Table 32b

Effect of Increasing $MgCO_3 \cdot 3H_2O$ and Lime on Removal of COD, TOC, and Total Phosphorus

JAR. NO.	DOSAGE IN mg/l			pH		ALK		STAB TO pH	ALK		HARDNESS			Ca.	Mg.	COD	TOC	T.P.			
	$MgCO_3$	Lime				OH	CO_3		CO_3	HCO_3	C	NC	T	as $CaCO_3$	as $CaCO_3$						
1	0	295						9.0	44	142			88	70	18	66	37	.33			
2	0	295						9.0	44	140			92	68	24	67	39	.33			
3	25	325						9.0	44	116			60	42	18	64	36	.14			
4	50	350						9.0	46	106			58	42	16	62	37	.12			
5	75	375						9.0	44	106			53	40	13	60	33	.11			
6	100	400						9.0	44	106			52	40	12	60	34	.11			

CHARACTERISTICS OF RAW WASTEWATER

ALKALINITY AS $CaCO_3$ 224
TOTAL HARDNESS AS $CaCO_3$ 108
CALCIUM AS $CaCO_3$ . . . 75
MAGNESIUM AS $CaCO_3$ . . 33
TOTAL COD 490
SOLUBLE COD . . . . . .
TOTAL TOC 156
SOLUBLE TOC . . . . . .
TOTAL BOD . . . . . .
SOLUBLE BOD . . . . .
NH_3-N .
$O-PO_4$.

Comments: Carbonation removes additional COD

Jar No.	Mg^{++} pptd (as $CaCO_3$)
1	15
2	15
3	32
4	52
5	72
6	91

Table 33

COD Reduction With and Without Addition of $MgCO_3 \cdot 3H_2O$*

JAR. NO.	DOSAGE IN mg/l			pH		ALK		STAB TO pH	ALK		HARDNESS			Ca.	Mg.	COD	% Removed				
	$MgCO_3$	Lime				OH	CO_3		CO_3	HCO_3	C	NC	T	as $CaCO_3$	as $CaCO_3$						
1	--	200		11.1		70	208						170	140	34	83	78				
2	70	210		11.1		76	228						196	124	72	76	80				
3	--	225		11.3		102	184						162	134	28	81	78				
4	70	235		11.3		100	192						182	120	62	68	82				
5	--	250		11.4		110	152						150	122	28	76	79				
6	70	265		11.4		118	164						176	122	54	66	83				

CHARACTERISTICS OF RAW WASTEWATER

ALKALINITY AS $CaCO_3$ ____________
TOTAL HARDNESS AS $CaCO_3$ ____________
CALCIUM AS $CaCO_3$ . . . ____________
MAGNESIUM AS $CaCO_3$ . . ____________
TOTAL COD . . . . . . ____________
SOLUBLE COD . . . . . ____________
TOTAL TOC . . . . . . ____________
SOLUBLE TOC . . . . . ____________
TOTAL BOD . . . . . . ____________
SOLUBLE BOD . . . . . ____________
NH_3-N . . . . ____________
O-PO_4 . . . . ____________

See next page for comments and analyses.

Table 33 (continued)

JAR. NO.	DOSAGE IN mg/l			pH		ALK		STAB TO pH	ALK		HARDNESS			Ca.	Mg.	COD	% Removed				
	$MgCO_3$	Lime				OH	CO_3		CO_3	HCO_3	C	NC	T	as $CaCO_3$	as $CaCO_3$						
7	--	275		11.5		134	128						140	124	16	74	80				
8	70	290		11.5		142	144						136	108	28	57	85				

*Grab sample Gainesville Municipal Waste

CHARACTERISTICS OF RAW WASTEWATER

ALKALINITY AS $CaCO_3$ 196 ($CO_3^=$ 28 HCO_3 168)
TOTAL HARDNESS AS $CaCO_3$ 98
CALCIUM AS $CaCO_3$ . . . 64
MAGNESIUM AS $CaCO_3$ . . 34
TOTAL COD 382
SOLUBLE COD . . . . . . ______
TOTAL TOC . . . . . . ______
SOLUBLE TOC . . . . . . ______
TOTAL BOD . . . . . . ______
SOLUBLE BOD . . . . . . ______
NH_3-N . . . . ______
$O-PO_4$ . . . . ______

Comments: 5 minutes @ 50 RPM - rapid mix
30 minutes @ 35 RPM - slow mix
Floc does not appear as large as with rapid mix (100 RPM) in all jars
From the appearance of floc and clarity we did not add enough $MgCO_3 \cdot 3H_2O$
Mg jars - much larger floc and settle faster
Faster filtering and much clearer on settling

Jar No.	Mg^{++} pptd
1	0
2	11
3	6
4	21
5	6
6	29
7	18
8	55

Table 34

COD Removal by Magnesium Carbonate Hydrolyzed With Lime

JAR. NO.	DOSAGE IN mg/l			pH		ALK		STAB TO pH	ALK		HARDNESS			Ca.	Mg.	COD					
	$MgCO_3$	Ca $(OH)_2$				OH	CO_3		CO_3	HCO_3	C	NC	T	as $CaCO_3$	as $CaCO_3$						
1	125	430		11.5		180	80	9.0	26	110	37	-99	37	32	5	64					
2	125	430		11.5		172	84	9.0	26	110	37	-99	37	32	5	67					
3	125	400		11.4		136	88	9.0	24	120	42	-102	42	34	8	69					
4	125	400		11.4		146	84	9.0	24	120	42	-102	42	34	8	72					
5	125	370		11.3		108	100	9.0	26	112	42	-96	42	30	12	72					
6	125	370		11.3		112	96	9.0	26	112	42	-96	42	30	12	73					

CHARACTERISTICS OF RAW WASTEWATER

ALKALINITY AS $CaCO_3$	188
TOTAL HARDNESS AS $CaCO_3$	92
CALCIUM AS $CaCO_3$	64
MAGNESIUM AS $CaCO_3$	28
TOTAL COD	374
SOLUBLE COD	
TOTAL TOC	
SOLUBLE TOC	
TOTAL BOD	
SOLUBLE BOD	
NH_3-N	
O-PO_4	

Comments:
Rapid mix - 5 minutes @ 70 RPM
Slow Mix - 30 minutes @ 40 RPM
All samples clear and bright - settled in 5 minutes
Duplicate filtered samples mixed for stabilization

Gainesville Raw 9:00 AM Grab sample

Jar No.	Mg^{++} pptd (as $CaCO_3$)
1-2	110
3-4	107
5-6	103

Table 35

COD Removal by Magnesium Carbonate Hydrolyzed With Lime

JAR. NO.	DOSAGE IN mg/l			pH		ALK		STAB TO pH	ALK		HARDNESS			Ca.	Mg.	COD					
	$MgCO_3$	Lime				OH	CO_3		CO_3	HCO_3	C	NC	T	as $CaCO_3$	as $CaCO_3$						
1	125	340		11.2		96	128	9.0	14	166	84	-82	84	42	42	76					
2	125	340		11.2		98	132	9.0	14	166	84	-82	84	42	42	76					
3	125	310		11.1		90	156	9.0	24	180	108	-72	108	48	60	80					
4	125	310		11.1		90	160	9.0	24	180	108	-72	108	48	60	80					
5	125	280		11.0		84	184	9.0	12	208	134	-74	134	52	82	89					
6	125	280		11.0		80	192	9.0	12	208	134	-74	134	52	82	91					

CHARACTERISTICS OF RAW WASTEWATER

ALKALINITY AS $CaCO_3$	188
TOTAL HARDNESS AS $CaCO_3$	92
CALCIUM AS $CaCO_3$	64
MAGNESIUM AS $CaCO_3$	28
TOTAL COD	374
SOLUBLE COD	
TOTAL TOC	
SOLUBLE TOC	
TOTAL BOD	
SOLUBLE BOD	
NH_3-N	
O-PO_4	

Comments:
Rapid mix @ 70 RPM - 5 minutes
Slow mix @ 40 RPM - 30 minutes
Rapidly settling floc - 5 minutes
Jars 1 and 2 - clear - slight yellow cast
Jars 3, 4, 5, 6 - yellow haze (cloudy)
This point of almost total removal of added Mg^{++} is clearly reflected in appearance of Jars 1-2 compared to Jars 3-4-5-6

Gainesville Raw Sewage 9:00 AM - grab sample collected 5/15/72

Jar No.	Mg^{++} pptd. (as $CaCO_3$)
1-2	73
3-4	55
5-6	33

Table 36

COD Removal by Magnesium Carbonate Hydrolyzed With Lime

JAR. NO.	DOSAGE IN mg/l			pH		ALK		STAB TO pH	ALK		HARDNESS			Ca.	Mg.	COD					
	$MgCO_3$	Lime				OH	CO_3		CO_3	HCO_3	C	NC	T	as $CaCO_3$	as $CaCO_3$						
1	125	430		11.6		162	76		24	100			34	32	2	56					
2	125	430		11.6		160	76														
3	125	400		11.5		140	80		20	110			42	36	6	58					
4	125	400		11.5		146	78														
5	125	370		11.4		126	80		16	116			42	34	8	61					
6	125	370		11.4		126	84									60					

CHARACTERISTICS OF RAW WASTEWATER

ALKALINITY AS $CaCO_3$ 186
TOTAL HARDNESS AS $CaCO_3$ 94
CALCIUM AS $CaCO_3$ . . . 62
MAGNESIUM AS $CaCO_3$ . . 32
TOTAL COD 520
SOLUBLE COD . . . . . . ______
TOTAL TOC . . . . ______
SOLUBLE TOC . . . . . . ______
TOTAL BOD . . . . ______
SOLUBLE BOD . . . . . . ______
NH_3 - N . . . . ______
O-PO_4 . . . . ______

Comments: Gainesville raw sewage 8:30 AM - grab sample
Sample collected 5/17/72

Mg Removed

Jars	Mg^{++} pptd (as $CaCO_3$)
1-2	118
3-4	114
5-6	112

Table 37

COD Removal, Duplicate Samples to Check Reproducibility of Results and Effect Mg^{++}

JAR. NO.	DOSAGE IN mg/l			pH		ALK		STAB TO pH	ALK		HARDNESS			Ca.	Mg.	COD						
	$MgCO_3$	Lime				OH	CO_3		CO_3	HCO_3	C	NC	T	as $CaCO_3$	as $CaCO_3$							
7	125	340		11.3		98	112		20	130	58	-92	58	32	26	62						
8	125	340		11.3		102	112									64						
9	125	310		11.2		88	140		20	150	86	-84	86	44	42	68						
10	125	310		11.2		90	140									68						
11	125	280		11.1		80	176		24	172	106	-90	106	48	58	76						
12	125	280		11.1		84	170									74						

CHARACTERISTICS OF RAW WASTEWATER

ALKALINITY AS $CaCO_3$ 186
TOTAL HARDNESS AS $CaCO_3$ 94
CALCIUM AS $CaCO_3$ . . . 62
MAGNESIUM AS $CaCO_3$ . . 32
TOTAL COD 520
SOLUBLE COD . . . . . .
TOTAL TOC . . . . . .
SOLUBLE TOC . . . . . .
TOTAL BOD . . . . . .
SOLUBLE BOD . . . . . .
NH_3 - N . . . .
O-PO_4 . . . .

Comments: Rapid mix - 5 minutes @ 70 RPM
Flocculation 30 minutes @ 40 RPM
Settling rapid in all jars <5 minutes
Supernatant clear
Excellent agreement between duplicate COD values and effect of ΔpH clearly evident

Gainesville grab sample - 8:30 AM

Mg removed (as $CaCO_3$)

Jars 7 and 8 - 94
Jars 9 and 10 - 78
Jars 11 and 12 - 62

Table 39

BOD, COD and TOC Reductions, Gainesville, Florida, Sewage

JAR. NO.	DOSAGE IN mg/l			pH		ALK		STAB TO pH	ALK		HARDNESS			Ca.	Mg.	COD	BOD	TOC			
	$MgCO_3$ $3H_2O$	Ca $(OH)_2$				OH	CO_3		CO_3	HCO_3	C	NC	T	as $CaCO_3$	as $CaCO_3$						
1	60	375		11.5		224	96	9.0					36	30	6	56	45	40			
2																					
3	80	400		11.5		230	100	9.0					56	46	10	53	44	39			
4																					
5	100	425		11.5		280	120	9.0					68	56	12	50	42	38			
6																					

CHARACTERISTICS OF RAW WASTEWATER

ALKALINITY AS $CaCO_3$	180
TOTAL HARDNESS AS $CaCO_3$	96
CALCIUM AS $CaCO_3$	52
MAGNESIUM AS $CaCO_3$	44
TOTAL COD	530
SOLUBLE COD	132
TOTAL TOC	105
SOLUBLE TOC	58
TOTAL BOD	161
SOLUBLE BOD	76
NH_3-N	
O-PO_4	

Comments: 5 minutes of rapid mix on Jars 1, 2
No rapid mix on Jar 3

Jar No.	% Reduction in COD Sol.	Ins.	Total
1	57	86	89
3	60	87	90
5	63	88	91

Mg Removed (as $CaCO_3$)

1 - 80
3 - 99
5 - 102

After Carbon and Clinoptilolite

Jar	TOC	COD	BOD
1	5	1.6	1.2
3	5	1.0	1.0
5	5	0.5	0.5

reductions in criteria values observed in other jar tests. The fact that final TOC values are higher than those for both COD and BOD could be due to the presence of an unusually stable organic compound or compounds not oxidized by hot dichromate or biodegraded in the BOD environment.

North Miami Wastewater

North Miami withdraws water very low in magnesium from shallow wells. However, upon receiving and analyzing this sample, the magnesium content was found to be very similar to the Gainesville wastewater. The magnesium present in the sewage probably results from the presence of a small amount of sea water entering the sewer lines. A test (Table 39) very similar to a previous jar test (Table 33) was conducted. The results again showed magnesium plus lime superior to lime alone in resultant COD residuals.

Table 40 compares the effectiveness of the magnesium process on two wastewaters run side by side. Sufficient $MgCO_3$ was added such that both contained the same amount. The North Miami wastewater behaves very much like waters observed in water treatment plants, in that alkalinity is less than total hardness. However, Gainesville exhibits a high negative noncarbonate hardness which is not affected by coagulation.

Table 41 continues the comparison of wastewaters run side by side. Again, the negative noncarbonate hardness is observed in the University of Florida sample, although at a much lower level. Finally, all three wastewaters were composited (Table 42) into one sample and the effect of mixing time and contact time at high pH were evaluated. All six samples were dosed similarly and subjected to identical times of rapid mixing. Then, at six different time periods of slow mixing, samples were withdrawn and COD determinations were made. The results show that 15 minutes slow mix is probably all that is required. The samples were then allowed to stand an additional two hours to evaluate the benefit of contact time at high pH. A significant reduction in COD was observed in all jars.

Wastewater Low in Magnesium

On May 18-19, 1972, two samples of raw wastewater from the Catoma Sewage Treatment Plant, Montgomery, Alabama, were obtained. One sample was collected at 3:00 A.M. and the other at 8:30 A.M. Analyses of the wastewaters showed only 3 mg/ℓ and 2 mg/ℓ of magnesium ion naturally present. Tables 43-47 present the jar tests conducted on these wastewaters. The 3:00 A.M. sample had a COD of 500 mg/ℓ while the 8:30 A.M. sample had a COD of 1,500 mg/ℓ, the highest COD encountered to date, and several times higher than normal municipal waste.

Table 39

North Miami Raw Sewage After Comminutor

JAR. NO.	DOSAGE IN mg/l			pH		ALK		STAB TO pH	ALK		HARDNESS			Ca.	Mg.	COD					
	$MgCO_3$	Lime				OH	CO_3		CO_3	HCO_3	C	NC	T	as $CaCO_3$	as $CaCO_3$						
1	--	285		11.1		54	108						170	150	20	33					
2	70	300		11.2		64	112						160	118	42	27					
3	0	315		11.3		71	108						165	150	15	32					
4	70	325		11.3		74	100						106	90	16	27					
5	0	325		11.4		114	88						130	120	10	32					
6	70	350		11.4		106	72						130	115	15	26					

CHARACTERISTICS OF RAW WASTEWATER

ALKALINITY AS $CaCO_3$	217
TOTAL HARDNESS AS $CaCO_3$	250
CALCIUM AS $CaCO_3$	220
MAGNESIUM AS $CaCO_3$	30
TOTAL COD	210
SOLUBLE COD	
TOTAL TOC	
SOLUBLE TOC	
TOTAL BOD	
SOLUBLE BOD	
NH_3-N	
O-PO_4	

Comments: 8:30 AM grab sample
Sample has little apparent color
compared to Gainesville
Jars 3,4,5,6, - milky; 1,2 - clear
To 5,6 added K_2SO_4 - cleared up jars 5,6
floc stringy before SO_4 added
floc bulky after SO_4 added
Jar 6 - bright
Jar 5 - hazy

Jar No.	Mg^{++} pptd (as $CaCO_3$)
1	10
2	37
3	15
4	63
5	20
6	64

Table 40

N. Miami Sewage - Compared with Gainesville Sewage

JAR. NO.	DOSAGE IN mg/l			pH	Turbidity	ALK		STAB TO pH	ALK		HARDNESS			Ca	Mg.	COD					
	$MgCO_3$	Ca $(OH)_2$				OH	CO_3		CO_3	HCO_3	C	NC	T	as $CaCO_3$	as $CaCO_3$						
1*	116	380		11.4	<1	108	56	9.0	12	62	74	30	104	84	20	21					
2*	116	400		11.5	<1	116	56	9.0	12	56	68	31	99	84	15						
3*	116	420		11.6	<1	146	40	9.0	10	56	66	30	96	80	16	20					
4**	92	300		11.3	>10	90	172	9.0	32	148	80	-100	80	44	36	>80					
5**	92	320		11.4	>10	94	156	9.0	28	144	72	-100	72	40	32						
6**	92	340		11.5	>10	106	136	9.0	24	142	60	-106	60	38	22	80					

*N. Miami
**Gainesville

CHARACTERISTICS OF RAW WASTEWATER

ALKALINITY AS $CaCO_3$	217*	206**
TOTAL HARDNESS AS $CaCO_3$	240*	100**
CALCIUM AS $CaCO_3$ . . .	216*	52**
MAGNESIUM AS $CaCO_3$ . .	24*	48**
TOTAL COD	210*	490**
SOLUBLE COD		
TOTAL TOC		
SOLUBLE TOC		
TOTAL BOD		
SOLUBLE BOD		
NH_3-N		
O-PO_4		

Comments: N. Miami sewage behaved as would a raw water being softened.
Gainesville sewage "negative NCH" came through unchanged.

Mg Precipitated (as $CaCO_3$)

Jar 1 - 85
2 - 90
3 - 89
4 - 76
5 - 80
6 - 90

Table 41

Comparison of Wastes from U. of Florida, Gainesville and N. Miami

JAR NO.	DOSAGE IN mg/l			pH		ALK		STAB TO pH	ALK		HARDNESS			Ca.	Mg.	COD	% Reduction				
	$MgCO_3$	$Ca(OH)_2$				OH	CO_3		CO_3	HCO_3	C	NC	T	as $CaCO_3$	as $CaCO_3$						
1*	117	350		11.4		136	64	9.0	12	62		-30	44	34	10	32	75				
2*	117	400		11.6		192	64	9.0	6	70		-32	44	36	8	28	80				
3**	117	400		11.5		116	120	9.0	22	122		-112	32	16	16						
4**	117	450		11.6		150	108	9.0	22	118		-108	32	22	10	60	88				
5***	140	425		11.5		122	64	9.0	12	62		28	102	88	14						
6***	140	450		11.6		184	28	9.0	10	50		28	88	78	10	14	90				

*U. of Florida - 14-hour composite.
**Gainesville, Fla. - grab.
***N. Miami - grab.

CHARACTERISTICS OF RAW WASTEWATER

ALKALINITY AS $CaCO_3$	134*	206**	217***
TOTAL HARDNESS AS $CaCO_3$	108*	100**	240***
CALCIUM AS $CaCO_3$	60*	52**	216***
MAGNESIUM AS $CaCO_3$	48*	48**	24***
TOTAL COD	130*	490**	210***
SOLUBLE COD			
TOTAL TOC			
SOLUBLE TOC			
TOTAL BOD			
SOLUBLE BOD			
NH_3-N			
O-PO_4			

Mg Precipitated (as $CaCO_3$)

Jar 1 - 120
2 - 122
3 - 114
4 - 120
5 - 118
6 - 122

Table 42

Mixture of Wastes of Gainesville, University of Florida and North Miami to Check Effect of Flocculation Time on Adsorption of COD

JAR. NO.	DOSAGE IN mg/l			pH	Turbidity	ALK		STAB TO pH	ALK		HARDNESS			Ca.	Mg.	COD	COD*				
	$MgCO_3$	Ca $(OH)_2$				OH	CO_3		CO_3	HCO_3	C	NC	T	as $CaCO_3$	as $CaCO_3$						
1	125	430		11.5	<1	128	96	9.0	12	62	46	-28	46	40	6	38	30				
2	125	430		11.6	<1	164	80	9.0	8	64	40	-32	40	32	8	36	30				
3	125	430		11.6	<1	152	80	9.0	11	79	60	-30	60	50	10	34	29				
4	125	430		11.6	<1	168	72	9.0	6	82	60	-28	60	50	10	34	29				
5	125	430		11.6	<1	168	72	9.0	12	66	44	-34	44	36	8	34	28				
6	125	430		11.6	<1	160	72	9.0	12	68	48	-32	48	38	10	34	27				

*COD determined again after 2 hrs. contact at high pH

Comments: The data indicate that:

(a) there is no increase in absorption of COD after 15 minutes flocculation

(b) two hours additional contact with pH 11.6 supernatant reduced COD about 7 ppm

CHARACTERISTICS OF RAW WASTEWATER

ALKALINITY AS $CaCO_3$ 174

TOTAL HARDNESS AS $CaCO_3$ 150

CALCIUM AS $CaCO_3$ . . . 102

MAGNESIUM AS $CaCO_3$ . . 48

TOTAL COD 360

SOLUBLE COD . . . . . . ______

TOTAL TOC . . . . . . ______

SOLUBLE TOC . . . . . ______

TOTAL BOD . . . . . . ______

SOLUBLE BOD . . . . . ______

NH_3-N . . . . ______

$O-PO_4$ . . . . ______

Treatment of Samples
5 min. at 70 RPM

1) 5 min. at 35
2) 10 min. at 35
3) 15 min. at 35
4) 30 min. at 35
5) 45 min. at 35
6) 60 min. at 35

Table 43

COD Reduction on Municipal Wastes of Montgomery, Alabama (Low Mg) With and Without Addition of $MgCO_3 \cdot 3H_2O$

JAR NO.	DOSAGE IN mg/l			pH	JTU Turbidity	ALK		STAB TO pH	ALK		HARDNESS			Ca.	Mg.	COD	Color				
	$MgCO_3$	$Ca(OH)_2$				OH	CO_3		CO_3	HCO_3	C	NC	T	as $CaCO_3$	as $CaCO_3$						
1	0	250		10.9	30	50	152	9.0	32	120	46	-106	46	38	8	76	30				
2	100	340		11.2	14	84	128	9.0	32	158	86	-104	86	14	72	66	20				
3	0	270		11.1	28	56	144	9.0	28	136	62	-102	62	54	8	72	30				
4	125	420		11.6	12	136	100	9.0	32	114	38	-108	38	28	10	60	7				
5	0	290		11.3	27	78	128	9.0	48	106	44	-110	44	36	8	70	30				
6	150	450		11.7	10	130	100	9.0	0	176	70	-106	70	66	4	56	5				

CHARACTERISTICS OF RAW WASTEWATER

ALKALINITY AS $CaCO_3$ ____________
TOTAL HARDNESS AS $CaCO_3$ ____________
CALCIUM AS $CaCO_3$ . . ____________
MAGNESIUM AS $CaCO_3$. ____________
TOTAL COD . . . . . . ____________
SOLUBLE COD . . . . . ____________
TOTAL TOC . . . . . . ____________
SOLUBLE TOC . . . . . ____________
TOTAL BOD . . . . . . ____________
SOLUBLE BOD . . . . . ____________
NH_3-N . . . . . . ____________
$O-PO_4$ . . . . . . ____________

See next page for comments and analyses.

Table 43 (continued)

JAR NO.	DOSAGE IN mg/l			pH	JTU Turbidity	ALK		STAB TO pH	ALK		HARDNESS			Ca	Mg	COD	Color				
	$MgCO_3$	$Ca(OH)_2$				OH	CO_3		CO_3	HCO_3	C	NC	T	as $CaCO_3$	as $CaCO_3$						
7	0	325		11.4	25	68	128	9.0	28	116	40	-104	40	32	8	68	27				
8	0	350		11.6	24	94	120	9.0	28	128	54	-102	54	46	8	66	27				

CHARACTERISTICS OF RAW WASTEWATER	
ALKALINITY AS $CaCO_3$	184
TOTAL HARDNESS AS $CaCO_3$	76
CALCIUM AS $CaCO_3$	64
MAGNESIUM AS $CaCO_3$	12
TOTAL COD	500
SOLUBLE COD	
TOTAL TOC	
SOLUBLE TOC	
TOTAL BOD	
SOLUBLE BOD	
NH_3-N	
$O-PO_4$	

Comments:
Jars 1,3,5,7,8 milky and colored
Jars 2,4,6 brilliant and clear, no visible color
Flocs 1,3,5,7,8 small, dense
Flocs 2,4,6 large, well formed, heavy
Samples 2,4,6 filtered much faster than 1,3,5
Estimate filtration rate for Mg^{++} samples 6 to 1 compared to no Mg^{++} samples

Mg precipitated (as $CaCO_3$)

Jar	Mg	Jar	Mg
1	4	5	4
2	10	6	-113
3	4	7	4
4	90	8	4

Table 44

COD Reduction on Municipal Wastes of Montgomery, Alabama (Low Mg)
With and Without $MgCO_3 \cdot 3H_2O$ Addition

JAR NO.	DOSAGE IN mg/l			pH	JTU Turbidity	ALK		STAB TO pH	ALK		HARDNESS			Ca	Mg	COD	Color				
	$MgCO_3$	Lime				OH	CO_3		CO_3	HCO_3	C	NC	T	as $CaCO_3$	as $CaCO_3$						
1	--	400		11.6	22	180	88	9.0	32	120			34	30	4	57	20				
2	--	500		11.8	20	260	100	9.0	48	102			34	30	4	61	20				
3	150	450		11.6	4	154	88	9.0	40	112			36	30	6	54	5				
4	175	475		11.6	5	154	96	9.0	24	120			26	24	2	54	5				
5	200	500		11.6	3	176	88	9.0	36	114			34	28	6	54	5				
6	225	525		11.6	3	176	88	9.0	32	124			44	36	8	53	5				

CHARACTERISTICS OF RAW WASTEWATER

ALKALINITY AS $CaCO_3$ 184
TOTAL HARDNESS AS $CaCO_3$ 76
CALCIUM AS $CaCO_3$ . . . 64
MAGNESIUM AS $CaCO_3$ . . 12
TOTAL COD 500
SOLUBLE COD . . . . . .
TOTAL TOC . . . . . .
SOLUBLE TOC . . . . . .
TOTAL BOD . . . . . .
SOLUBLE BOD . . . . . .
NH_3-N . . . .
O-PO_4 . . . .

Comments: Rapid Mix - 5 minutes @ 70 RPM
Slow Mix - 30 minutes @ 40 RPM
Jars 1,2 - slow settling - yellow milky cast
Jars 3,4,5,6 - rapid settling - clear and bright
10 minutes settling prior to collecting turbidity samples 2" below surface using special sampler pipette
Mg precipitation relatively small effect on COD removal in this test. Color removal excellent. Suspended solids removed, practically 99%+.
Sample collected 3:00 AM 5-19-72.

Mg Precipitated (as $CaCO_3$)

Jar 1 - 8 Jar 4 - 132
2 - 8 5 - 146
3 - 111 6 - 162

Table 45

COD Reduction on Municipal Wastes of Montgomery, Alabama

JAR. NO.	DOSAGE IN mg/l			pH	Turbidity	ALK		STAB TO pH	ALK		HARDNESS			Ca.	Mg.	COD	Color				
	$MgCO_3$	Ca $(OH)_2$				OH	CO_3		CO_3	HCO_3	C	NC	T	as $CaCO_3$	as $CaCO_3$						
1	0	400		11.2	42			9.0	40	188			70	60	10	250	60				
2	150	400		11.1	20			9.0	44	214			108	80	28	240	42				
3	0	425		11.4	37			9.0	80	140			80	70	10	250	60				
4	150	425		11.3	20			9.0	68	192			104	80	24	220	40				
5	0	450		11.6	37			9.0	72	146			66	60	6	250	60				
6	150	450		11.4	6			9.0	52	168			62	40	22	190	30				

CHARACTERISTICS OF RAW WASTEWATER

ALKALINITY AS $CaCO_3$ 216
TOTAL HARDNESS AS $CaCO_3$ 54
CALCIUM AS $CaCO_3$ . . . 46
MAGNESIUM AS $CaCO_3$ . . 10
TOTAL COD 1,700
SOLUBLE COD . . . . . . ______
TOTAL TOC . . . . ______
SOLUBLE TOC . . . . . . ______
TOTAL BOD . . . . ______
SOLUBLE BOD . . . . . . ______
NH_3-N . . . . ______
$O-PO_4$ . . . . ______

Comments: All flocs smaller than usual
Jars 1,3,5 very cloudy
Jars 2,4 cloudy but less than 1,3,5
Jar 6 almost clear, slight haze
Samples carbonated and filtered for analysis
Did not add enough lime to precipitate
the magnesium

Mg Precipitated (as $CaCO_3$)

Jar 1 - 0
2 - 87
3 - 0
4 - 91
5 - 4
6 - 93

5-minute settling

1 - very poor
2 - poor
3 - very poor
4 - fair
5 - very poor
6 - good

Table 46

COD Removal by Magnesium Carbonate Hydrolyzed with Lime

JAR. NO.	DOSAGE IN mg/l			pH	Turbidity	ALK		STAB TO pH	ALK		HARDNESS			Ca.	Mg.	COD	Color				
	$MgCO_3$	Lime				OH	CO_3		CO_3	HCO_3	C	NC	T	as $CaCO_3$	as $CaCO_3$						
1	0	450		11.5	35			9.0	68	176			72	66	6	215	60				
2	150	450		11.3	10			9.0	92	160			82	60	22	180	40				
3	150	475		11.4	7			9.0	64	180			68	60	8	178	40				
4	175	500		11.4	5			9.0	88	154			64	54	10	180	35				
5	200	525		11.4	4			9.0	80	150			56	46	10	179	30				
6	0	525		11.7	30			9.0	108	134			72	70	2	212	60				

CHARACTERISTICS OF RAW WASTEWATER

ALKALINITY AS $CaCO_3$ 216
TOTAL HARDNESS AS $CaCO_3$ 54
CALCIUM AS $CaCO_3$ . . 46
MAGNESIUM AS $CaCO_3$ . . 8
TOTAL COD 1,700
SOLUBLE COD . . . . . . ______
TOTAL TOC . . . . . . ______
SOLUBLE TOC . . . . . . ______
TOTAL BOD . . . . . . ______
SOLUBLE BOD . . . . . . ______
NH_3-N . . . . ______
O-PO_4 . . . . ______

Comments: Only 1 hour contact time at high pH
Did not attain pH of 11.6
Montgomery, Alabama, Catoma Plant,
8:30 AM grab sample, raw sewage
Color - 80

Mg Precipitated as $CaCO_3$

Jar 1 - 2
2 - 91
3 - 105
4 - 120
5 - 138
6 - 6

Table 47

COD Removal by Magnesium Carbonate Hydrolyzed with Lime

JAR NO.	DOSAGE IN mg/l			pH	Turbidity	ALK		STAB TO pH	ALK		HARDNESS			Ca.	Mg.	COD	Color				
	$MgCO_3$	Lime				OH	CO_3		CO_3	HCO_3	C	NC	T	as $CaCO_3$	as $CaCO_3$						
1	150	510		11.6	6								46	42	4	140	35				
2	200	560		11.5	6								42	40	2	130	35				
6	100	--		11.4	5								38	24	14	140	35				

CHARACTERISTICS OF RAW WASTEWATER

ALKALINITY AS $CaCO_3$	216
TOTAL HARDNESS AS $CaCO_3$	54
CALCIUM AS $CaCO_3$	46
MAGNESIUM AS $CaCO_3$	8
TOTAL COD	1,700
SOLUBLE COD	
TOTAL TOC	
SOLUBLE TOC	
TOTAL BOD	
SOLUBLE BOD	
NH_3-N	
O-PO_4	

Comments: Rapid Mix -70 RPM - 5 minutes
Slow Mix - 40 RPM - 25 minutes
Settling - 10 minutes - sample for turbidity
Standing - 2 hours - sample for COD
Supernatant remaining in the 2 jars was composited to yield 1 liter - a second dosage of $MgCO_3$ was then added (Jar 6) - flocculated, settled, and filtered
Montgomery, Alabama, 8:30 AM grab,raw
Color - 135

Mg pptd (as $CaCO_3$)

Jar 1 - 131
2 - 151

Before discussing these most interesting samples, two very important parameters need to be brought into the evaluation of the magnesium process. As early as October, 1971, the consistent superiority of the magnesium process over lime alone had been visually observed in the clarity of the jars containing magnesium. Heretofore, color and turbidity removal had been only visually observed. Beginning with Table 42, color and turbidity measurements are now being included to demonstrate analytically these additional advantages previously observed.

Tables 43 and 44 show conclusively the advantages of the magnesium coagulation process over lime alone. Although the COD difference between the two processes is small on this wastewater, the color and turbidity differences are vastly significant.

Tables 45 and 46 point out perhaps the most significant finding to date, namely, the higher the COD the greater the removal of COD by magnesium and lime over lime alone. Again, color and turbidity removals are superior using the magnesium process against lime alone. The desired pH range of 11.5-11.6 was not attained during these tests using the magnesium process. Therefore, another sample was obtained to further investigate this high COD wastewater and to evaluate COD reduction by the magnesium ion (as in Tables 34-37).

Table 47 represents a brief test involving double flocculation in an attempt to utilize the excess hydroxide gained in the first coagulation. Any advantage to be realized by this procedure is not evident in this test. The COD values for coagulated, filtered and stabilized effluent for jars 1 and 2 of this test are even lower than those in Table 45 and about 70 mg/ℓ lower than when lime alone is used.

A third sample of the Montgomery, Alabama, wastewater was received and showed only 2 mg/ℓ natural magnesium, a COD of 1,400 mg/ℓ, and a color of 160. Tables 48-49 show the results of the jar tests. Table 48 contains, in addition, final granular carbon filtration. The reduction in COD from 1,400 to 4 mg/ℓ and color from 160 to 0 mg/ℓ demonstrates the high quality effluent which may be obtained by physical-chemical treatment of municipal wastes. The mg/ℓ COD removed/mg/ℓ magnesium ion precipitated averaged 36.0 for the 12 jars.

Montgomery waste is the only one readily available whose magnesium content is so low as to be negligible and which may be employed to secure a family of "lime only" base line curves covering a rather wide range of COD and BOD values in the untreated waste.

The data obtained in Table 50 must be compared with those of Table 51 and Table 52 which follow. In Table 51, 50 ppm $MgCO_3 \cdot 3H_2O$ is used in all jars and in Table 52, 100 ppm of $MgCO_3 \cdot 3H_2O$ is used. First, to compare the data of Tables 50 and 51 only. In doing so, the data from the jars as shown below should be compared.

Table 48

COD Reduction by Magnesium Carbonate and Lime Using Montgomery, Alabama, Raw Sewage

NO.	DOSAGE IN mg/l			pH	Turbidity	ALK		STAB TO pH	ALK		HARDNESS			Ca	Mg	Color*	COD*	COD**	Color**		
	$MgCO_3$	Lime				OH	CO_3		CO_3	HCO_3	C	NC	T	as $CaCO_3$	as $CaCO_3$						
1	200	550		11.4	3	140	132	9.0	56	150			52	46	6	20	156	16	0		
2	200	550		11.4	3	142	131	9.0								20	152				
3	200	570		11.5	4	155	139	9.0	64	146			46	42	4	20	140	8	0		
4	200	570		11.5	4	156	140	9.0								20	142				
5	200	590		11.6	4	166	148	9.0	66	140			40	38	2	20	136	4	0		
6	200	590		11.6	4	165	146	9.0								20	134				

*After coagulation - settling- standing - filtration Whatman #2

**As shown (*) plus granular activated carbon prior to carbonation

CHARACTERISTICS OF RAW WASTEWATER

ALKALINITY AS $CaCO_3$ 168

TOTAL HARDNESS AS $CaCO_3$ 60

CALCIUM AS $CaCO_3$ 52

MAGNESIUM AS $CaCO_3$ 8

TOTAL COD 1,400

SOLUBLE COD

TOTAL TOC

SOLUBLE TOC

TOTAL BOD

SOLUBLE BOD

NH_3 - N

O-PO_4

Comments: Collected 8:30 AM 6/15/72
5 minutes rapid mix @ 70 RPM
20 minutes slow mix @ 40 RPM
2 hours standing
All jars have large and heavy flocs - rapid settling, <5 minutes - supernatant bright and clear
Turbidity samples taken 10 minutes after slow mix stopped
Carbon column - 2" diameter, 15" deep, and 210 mls/minute flow rate
Color - 160; Turbidity - 65

Mg Precipitated as $CaCO_3$

Jars 1&2 - 142
3&4 - 144
5&6 - 146

Table 49

COD Reduction by Magnesium Carbonate and Lime Using Montgomery, Alabama, Raw Sewage

JAR. NO.	DOSAGE IN mg/l			pH	Turbidity	ALK		STAB TO pH	ALK		HARDNESS			Ca.	Mg.	COD					
	$MgCO_3$	Lime				OH	CO_3		CO_3	HCO_3	C	NC	T	as $CaCO_3$	as $CaCO_3$						
1	200	490		11.1	10	70	172						30	12	18	188					
2	200	490		11.1	10																
3	200	510		11.2	9	96	164						30	14	16	180					
4	200	510		11.2	9																
5	200	530		11.3	7	118	158						26	16	10	168					
6	200	530		11.3	7																

CHARACTERISTICS OF RAW WASTEWATER

ALKALINITY AS $CaCO_3$ 168
TOTAL HARDNESS AS $CaCO_3$ 60
CALCIUM AS $CaCO_3$ . . . 52
MAGNESIUM AS $CaCO_3$ . . 8
TOTAL COD 1,400
SOLUBLE COD . . . . .
TOTAL TOC . . . . . .
SOLUBLE TOC . . . . .
TOTAL BOD . . . . . .
SOLUBLE BOD . . . . .
NH_3-N . . . .
$O-PO_4$ . . . .

Comments: Rapid Mix - 5 minutes @ 70 RPM
Slow Mix - 20 minutes @ 40 RPM
Settling - 10 minutes
Standing - 90 minutes
Color - 160

Mg Precipitated as $CaCO_3$

Jars 1&2 - 130
3&4 - 132
5&6 - 138

Table 50

Treatment of Montgomery, Alabama, Waste with Lime Alone, High COD Waste

JAR. NO.	DOSAGE IN mg/l			pH	Turbidity	ALK		STAB TO pH	ALK		HARDNESS			Ca.	Mg.	COD	% Removed	TOC	%Removed	Color	
	$MgCO_3$ $3H_2O$	Ca $(OH)_2$				OH	CO_3		CO_3	HCO_3	C	NC	T	as $CaCO_3$	as $CaCO_3$						
1	0	400		11.1	30	114	124	9.0	34	204						180	82	54	60	70	
2	0	415		11.2	30	162	124	9.0	74	174						180	82			70	
3	0	430		11.3	24	200	116	9.0	78	172						165	83			60	
4	0	450		11.4	20	188	108	9.0	48	186						160	83	49	64	60	
5	0	500		11.5	15	238	104	9.0	106	120						150	85			50	
6	0	550		11.6	15	294	108	9.0	64	162						135	86	37	72	40	

CHARACTERISTICS OF RAW WASTEWATER

ALKALINITY AS $CaCO_3$ 220
TOTAL HARDNESS AS $CaCO_3$ 64
CALCIUM AS $CaCO_3$ . . . 50
MAGNESIUM AS $CaCO_3$ . . 14
TOTAL COD 985
SOLUBLE COD 380
TOTAL TOC 137
SOLUBLE TOC 50
TOTAL BOD . . . . . .
SOLUBLE BOD . . . . .
NH_3-N . . . . . .
O-PO_4 . . . . . .

Comments: Flocs small, settling poor
Sample filtration slow

Jar No.	% Reduction in COD Sol.	Ins.	Total
1	53	70	82
2	53	70	82
3	57	73	83
4	58	74	84
5	60	76	85
6	65	78	87

Color - 85

Table 51

Treatment of Montgomery, Alabama, Waste with Lime and 50 ppm $MgCO_3 \cdot 3H_2O$, High COD

JAR. NO.	DOSAGE IN mg/l			pH	Turbidity	ALK		STAB TO pH	ALK		HARDNESS			Ca.	Mg.	COD	% Removed	TOC	% Removed	Color	
	$MgCO_3$ $3H_2O$	Ca $(OH)_2$				OH	CO_3		CO_3	HCO_3	C	NC	T	as $CaCO_3$	as $CaCO_3$						
1	50	400		11.1	16	136	132	9.0	24	184			58	40	18	111	89	36	73	32	
2	50	440		11.2	11	144	124	9.0	50	140			32	16	16	108	89	35	74	27	
3	50	475		11.4	9	166	108	9.0	30	154			24	16	8	102	90	33	75	20	
4	50	550		11.7	--	204	116	9.0	50	120			24	14	10	116	88	38	72	15	

CHARACTERISTICS OF RAW WASTEWATER

ALKALINITY AS $CaCO_3$	220
TOTAL HARDNESS AS $CaCO_3$	64
CALCIUM AS $CaCO_3$	50
MAGNESIUM AS $CaCO_3$	14
TOTAL COD	985
SOLUBLE COD	380
TOTAL TOC	137
SOLUBLE TOC	50
TOTAL BOD	
SOLUBLE BOD	
NH_3-N	
O-PO_4	

Jar	Mg Precipitated as $CaCO_3$
1	31
2	33
3	41
4	74

Supernatant	Jar No.	% Reduction in COD Sol.	Ins.	Total
1 - very cloudy	1	71	81	89
2 - cloudy	2	72	82	89
3 - cloudy	3	73	83	90
4 - bright	4	70	80	88

Color - 85

Table 52

Treatment of Montgomery, Alabama, Waste with Lime and 100 ppm $MgCO_3 \cdot 3H_2O$, High COD

JAR. NO.	DOSAGE IN mg/l			pH	Turbidity	ALK		STAB TO pH	ALK		HARDNESS			Ca.	Mg.	COD	% Removed	TOC	% Removed	Color	
	$MgCO_3$ $3H_2O$	Ca $(OH)_2$				OH	CO_3		CO_3	HCO_3	C	NC	T	as $CaCO_3$	as $CaCO_3$						
1	100	425		11.1	9	128	128	9.0	44	152			38	20	18	98	90	34	75	25	
2	100	465		11.2	7	146	108	9.0	36	150			28	16	12	100	90	32	76	20	
3	100	500		11.4	5	172	96	9.0	40	144			22	16	6	97	90	30	78	15	
4	100	550		11.6	-	184	120	9.0	36	136			24	16	8	109	89	35	74	15	

CHARACTERISTICS OF RAW WASTEWATER	
ALKALINITY AS $CaCO_3$	220
TOTAL HARDNESS AS $CaCO_3$	64
CALCIUM AS $CaCO_3$	50
MAGNESIUM AS $CaCO_3$	14
TOTAL COD	985
SOLUBLE COD	380
TOTAL TOC	137
SOLUBLE TOC	50
TOTAL BOD	
SOLUBLE BOD	
NH_3-N	
$O-PO_4$	

Jar	Mg Precipitated as $CaCO_3$	Supernatant
1	66	cloudy
2	72	bright
3	78	bright
4	76	bright

Color - 85

Table 50	Table 51
Jar No. 1	Jar No. 1
Jar No. 2	Jar No. 2
Jar No. 4	Jar No. 3
Jar No. 6	Jar No. 4

Jar No.	COD Table 50	Jar No.	COD Table 51	% Reduction in Residual COD from Lime Treatment Due to 50 ppm $MgCO_3$
1	180	1	111	38
2	180	2	108	38
4	160	3	102	36
6	135	4	116	14

The lower percentage reduction at the very high pH 11.7 is probably due to stabilization of insoluble COD by the large excess of lime at this pH value. This is consistent with the fact that values for turbidity and color are not affected but steadily improve as Mg precipitated and pH increased.

Table 52 is a repeat of Table 51 but with the dosage of $MgCO_3 \cdot 3H_2O$ doubled to 100 ppm. The resulting values for COD and TOC, and corresponding percentage reductions, are only slightly better than for 50 mg/ℓ $MgCO_3 \cdot 3H_3O$, indicating that for this type of waste, the optimum dosage of $MgCO_3 \cdot 3H_3O$ is slightly greater than 50 ppm and much less than 100 ppm. The percentage reduction figures perhaps show it best.

Jar No.	COD Table 51	Jar No.	COD Table 52	% Reduction in Residual COD from Lime Treatment Due to Add. 50 ppm $MgCO_3 \cdot 3H_2O$
1	111	1	98	10
2	108	2	100	8
3	102	3	97	10
4	116	4	109	9

To further substantiate the value of the magnesium ion in coagulating raw sewage, samples of low magnesium wastewater were secured for jar testing. Tables 53 and 54 demonstrate the effect or lack of effect of the added magnesium ion. The wastewater was collected at the Catoma Sewage Treatment Plant at Montgomery, Alabama. Table 53 was performed using a high COD wastewater and Table 54 utilized a low COD wastewater.

Table 53 employed a narrow range of precipitated magnesium. A wider range would have been better, as noted below. The superiority of the magnesium and lime treatment over lime alone is shown by COD

Table 53

Coagulation of Low Magnesium, High COD Waste, Montgomery, Alabama

JAR. NO.	DOSAGE IN mg/l			pH		ALK		STAB TO pH	ALK		HARDNESS			Ca.	Mg.	COD	Color				
	$MgCO_3$ $3H_2O$	Ca $(OH)_2$				OH	CO_3		CO_3	HCO_3	C	NC	T	as $CaCO_3$	as $CaCO_3$						
1	80	400		11.1		68	208							50	26	152	20				
2	80	420		11.2		88	176							40	20	132	15				
3	80	430		11.3		94	168							36	18	126	10				
4	80	450		11.4		112	140							36	12	118	5				
5	80	460		11.5		126	124							24	12	115	5				
6	--	450		11.5		138	152							34	12	161	40				

CHARACTERISTICS OF RAW WASTEWATER

ALKALINITY AS $CaCO_3$	212
TOTAL HARDNESS AS $CaCO_3$	50
CALCIUM AS $CaCO_3$ . . .	38
MAGNESIUM AS $CaCO_3$ . .	12
TOTAL COD	1,450
SOLUBLE COD	341
TOTAL TOC	
SOLUBLE TOC	
TOTAL BOD	
SOLUBLE BOD	
NH_3-N	
O-PO_4	

Jar	Mg Precipitated as $CaCO_3$
1	44
2	50
3	52
4	58
5	58
6	0

Color - 80

Table 54

Coagulation of Low Magnesium, Low COD Waste, Montgomery, Alabama

JAR NO.	DOSAGE IN mg/l			pH		ALK		STAB TO pH	ALK		HARDNESS			Ca.	Mg.	COD	Color				
	$MgCO_3$ $3H_2O$	$Ca(OH)_2$				OH	CO_3		CO_3	HCO_3	C	NC	T	as $CaCO_3$	as $CaCO_3$						
1	100	280		11.2											56	47	10				
2	100	300		11.3											48	45	10				
3	100	325		11.4											38	40	7				
4	100	340		11.5											12	35	5				
5	100	360		11.6											12	40	5				
6	--	360		11.8											12	50	15				

CHARACTERISTICS OF RAW WASTEWATER	
ALKALINITY AS $CaCO_3$	196
TOTAL HARDNESS AS $CaCO_3$	144
CALCIUM AS $CaCO_3$	132
MAGNESIUM AS $CaCO_3$	12
TOTAL COD	197
SOLUBLE COD	136
TOTAL TOC	
SOLUBLE TOC	
TOTAL BOD	
SOLUBLE BOD	
NH_3-N	
O-PO_4	

Comments: Jars 1,5 progressively clearer
Jar 6 cloudy
Color - 30

Jar	Mg Precipitated as $CaCO_3$
1	30
2	38
3	48
4	74
5	74
6	0

and color analyses. Comparison of Table 53 with Tables 48 and 49 show that a much lower dosage of magnesium is about as effective as the massive dosages of Tables 48 and 49, and far less lime is required. This fact was shown in Tables 51 and 52 also.

Jar test data collected using low magnesium wastewaters have been for medium and high strength COD concentrations. A low strength COD wastewater was desired to complete the picture on the effect of the magnesium ion. Table 54 represents this testing program. This type of wastewater would be encountered at most plants during the early morning hours, holidays and weekends. The data indicate that during these periods treatment with lime only would be sufficient. A plant which has a substantial amount of magnesium in its raw water would add lime to precipitate the magnesium for storage and recycling. A plant having wastewater low in magnesium would not add magnesium during these low COD periods. Several other samples of this type of wastewater will be tested in the future.

The higher the raw COD the more beneficial is the magnesium ion. A wastewater having a COD greater than 2,000 needs to be examined to further substantiate this repetitious finding.

Precipitation of Metals

An analysis of six metals was accomplished using raw sewage from Montgomery, Alabama. The sewage was subjected to coagulation, sand filtration, carbon adsorption, and ion exchange by clinoptilolite. The raw COD was 1,400 mg/ℓ and the final COD was 4 mg/ℓ.

Metal	Raw Sewage (mg/ℓ)	Treated (mg/ℓ)
Copper	0.06	<0.01
Zinc	0.33	0.02
Lead	0.07	<0.05
Total Mercury	0.000012	0.000004
Barium	0.43	<0.10
Aluminum	0.91	<0.20

The low solubility of most metallic hydroxides at high pH values suggests the application of the magnesium treatment process to industrial wastes high in metallic ions for recovery of valuable raw materials as well as meeting effluent standards.

SECTION VI. PILOT PLANT STUDIES

Pilot Plant

Figure 1 is a flow sheet of the pilot plant and Table 55 gives the dimensions and capacity in gallons of each of the main units. Two 50 gpm pumps were mounted in parallel on a steel framework below the surface of the influent wastewater in the comminutor discharge basins of the waste treatment plant of the city of Gainesville, Florida. When operating, they served as a continuous sampler, discharging untreated waste into flow control (1) which is a baffled steel tank fitted with an adjustable V-notch weir which could be set for any desired flow up to 100 gpm. Excess waste was returned to the comminutor basin through a drain pipe. This makes it possible to operate at any desired rate up to 100 gpm.

Recycled magnesium bicarbonate liquor from storage tank (11) was pumped by a calibrated positive displacement pump and added to the waste as it discharged from the weir. The waste flowed by gravity through a small rectangular baffled steel trough to rapid mixing basin (2) and then to the bottom of the flocculator (3). Lime slurry (12) was added in the discharge line between the rapid mix and flocculator. Much experience with the large, heavy flocs formed by the reaction between the magnesium and the lime soon indicated that the rapid mix was not needed, as the large heavy flocs formed a fluidized bed at the flocculator paddle speed of 1-2 rpm.

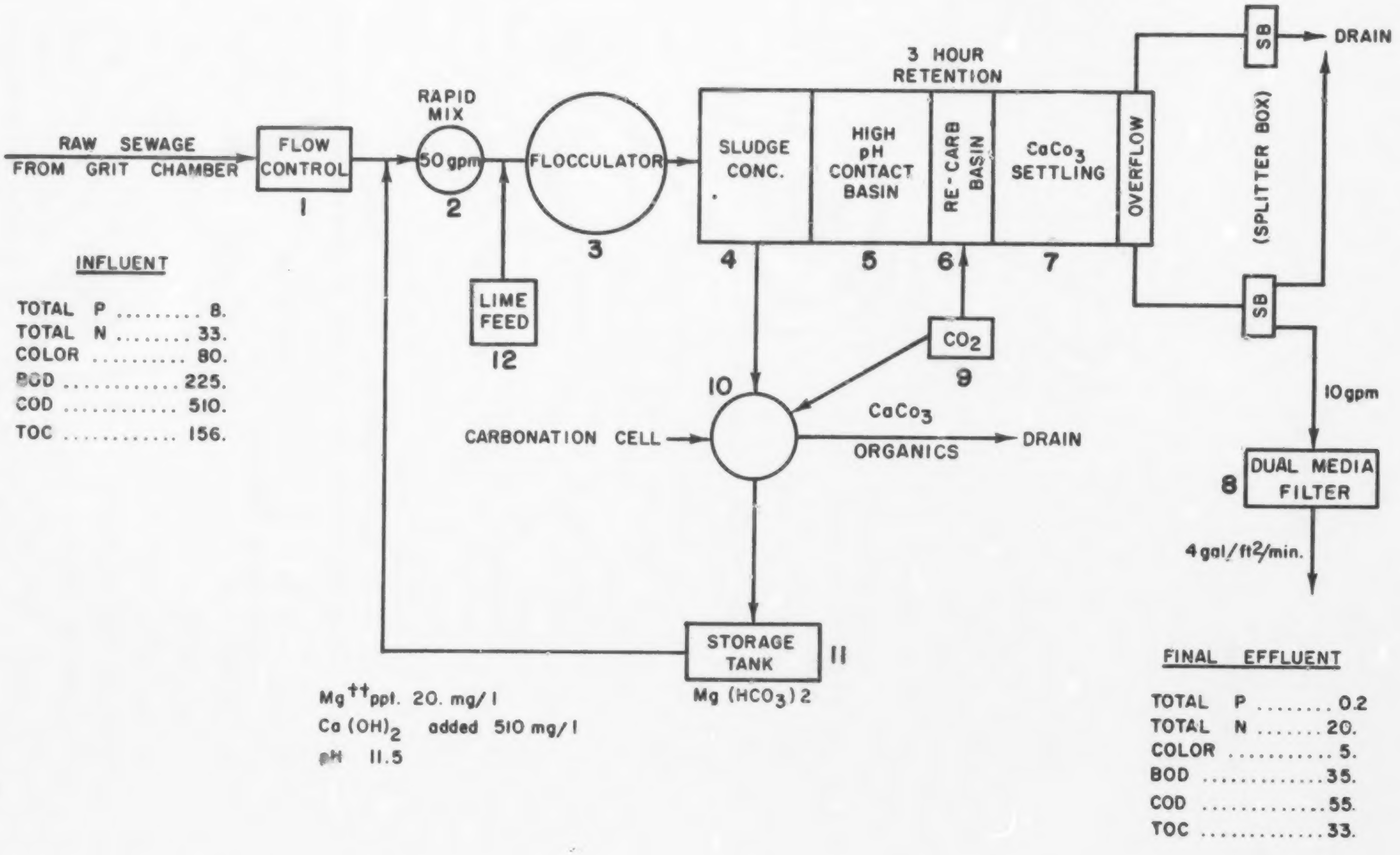
The coagulated and flocculated slurry passed to twin sludge concentrators (4) and the clear settled effluent passed to a baffled settling basin. Baffles provided a high pH contact basin (5), a central carbonation basin (6) and a secondary settling basin (7) to remove most of the $CaCO_3$ precipitated in the carbonation basin.

Table 55

Dimensons of Main Units

Unit	Dimensons	Volume (cu ft)	Volume (gal)
Mix basin	30" × 30" × 5'	30	225
Flocculation	7' × 8'10"	335	2,500
Sludge concentration	9'3" × [illegible]'8" × 6'	335	2,500
High pH contact basin	11' × 9'3" × 8'7"	865	6,588
Carbonation basin	3' × 9'3" × 8'7"	236	1,770
$CaCO_3$ settling basin	10' × 9'3" × 8'7"	786	5,895

FIGURE I
PILOT PLANT FLOW SCHEME


RAW SEWAGE
FROM GRIT CHAMBER
FLOW CONTROL
1
RAPID MIX
50 gpm
2
LIME FEED
12
FLOCCULATOR
3
3 HOUR RETENTION
SLUDGE CONC.
4
HIGH pH CONTACT BASIN
5
RE-CARB BASIN
6
CaCo3 SETTLING
7
OVERFLOW
SB
(SPLITTER BOX)
SB
DRAIN
10gpm
DUAL MEDIA FILTER
8
4 gal/ft2/min.
CO2
9
10
CARBONATION CELL
CaCo3
ORGANICS
DRAIN
STORAGE TANK
11
Mg (HCO3) 2
Mg++ppt. 20. mg/l
Ca (OH)2 added 510 mg/l
pH 11.5

INFLUENT

TOTAL P	8.
TOTAL N	33.
COLOR	80.
BOD	225.
COD	510.
TOC	156.

FINAL EFFLUENT

TOTAL P	0.2
TOTAL N	20.
COLOR	5.
BOD	35.
COD	55.
TOC	33.

The settled effluent passed to an effluent trough with ten equally spaced V-notches on the receiving side and open at both ends. A movable baffle made it possible to divide the effluent flow into any two desired multiples of 10 percent. These two flows passed to splitter boxes, each provided with an adjustable weir by which the flows could be further divided when desired. In practice, the flow of one splitter box passed to waste and the other passed through a dual-media filter (8) of sand capped with anthrafilt and operated at a rate of 4 gal/ft^2/min. Figure 2 is a view of the pilot plant.

Magnesium Recovery

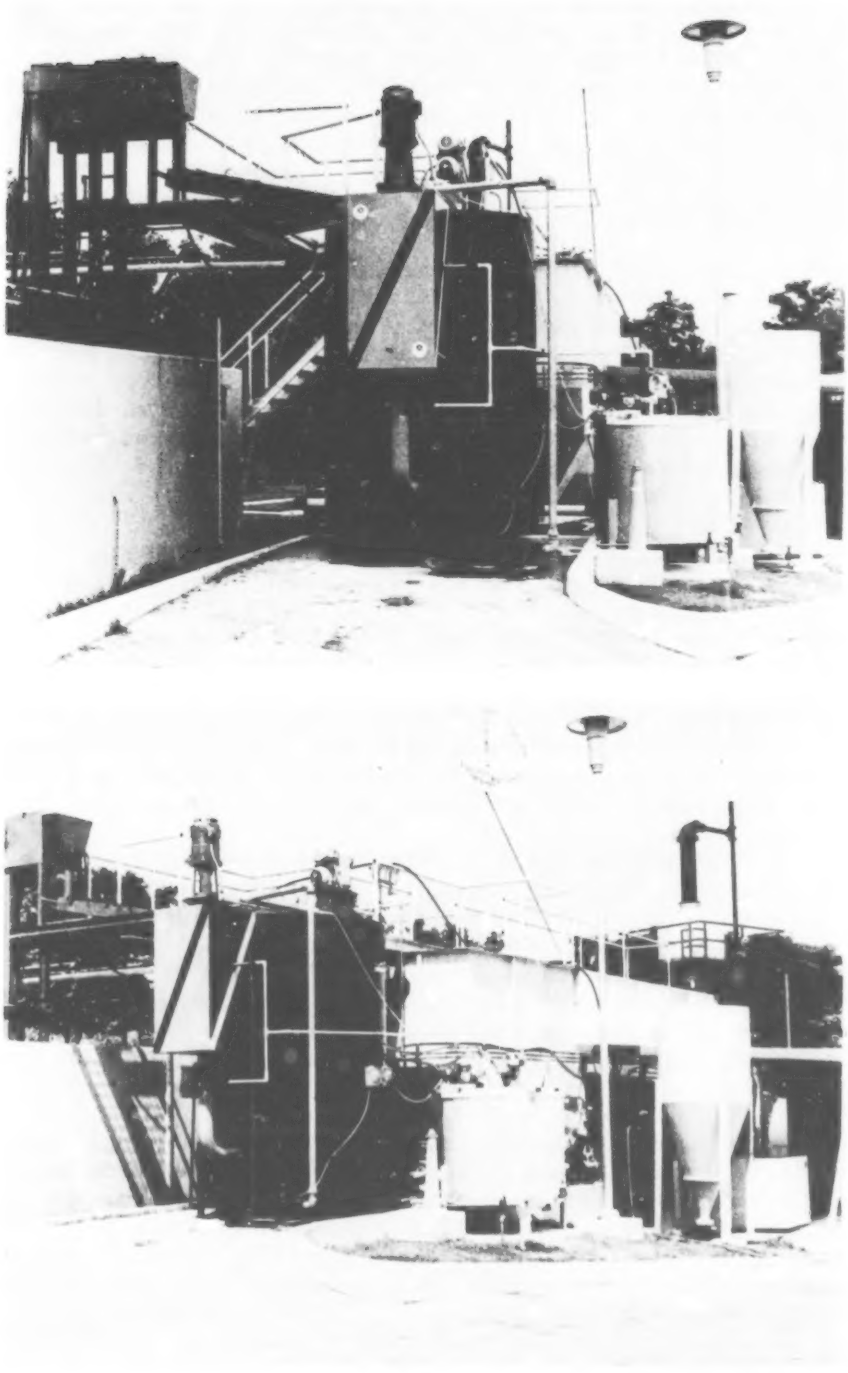
Sludge carbonation for magnesium recovery and recycling was carried out on a "batch" basis. Settled sludge from the twin concentrators (4) was drawn by gravity into a 175 gal carbonation tank (10) equipped with a rapid mix impeller. Pure CO_2 from a refrigerated storage unit (9) supplied by the Chemetron Corporation was passed through a calibrated flow meter into the rapidly mixed slurry until the pH was reduced to pH 7.5. The carbonated sludge was allowed to settle and the supernatant transferred to storage tank (11) and its alkalinity as $CaCO_3$ determined for each batch.

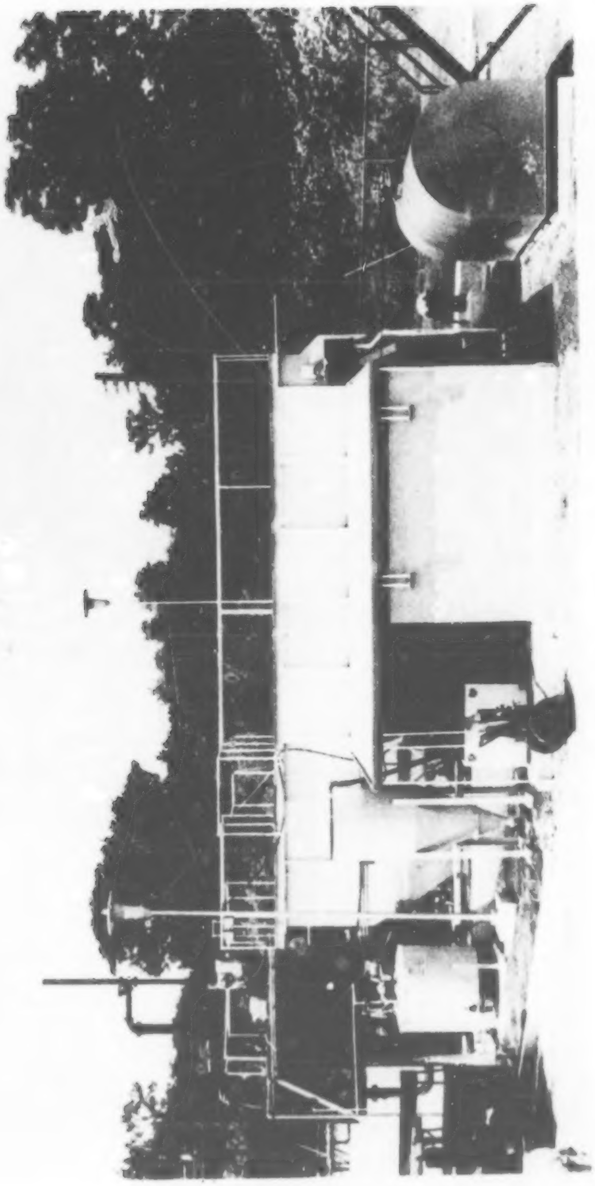
The procedure described above for the recovery of the magnesium is not desirable since the dissolution of the $Mg(OH)_2$ component of the sludge flocs by CO_2 releases at least part of the trapped organics and inorganics. This was not a serious problem using pure CO_2 since alkalinity values of the magnesium liquor as high as 25,000-30,000 ppm as $CaCO_3$ were obtained. The volume of this very rich magnesium liquor to be returned as magnesium make-up was relatively small. However, in actual practice, and using kiln gas containing only 20 percent CO_2, the maximum alkalinity to be obtained is 16,000 ppm as $CaCO_3$, thus requiring more recycled magnesium liquor.

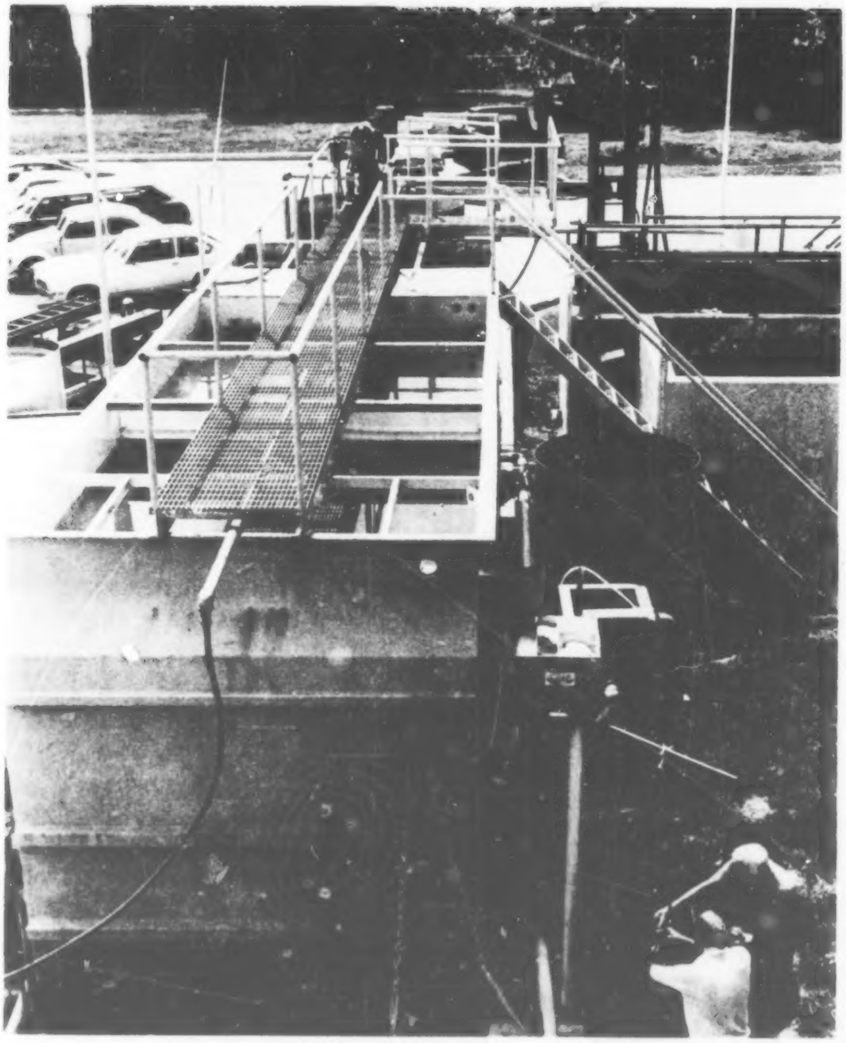
In actual practice, the thickened sludge will pass to a vacuum filter. The clarified filtrate will be recycled to the influent waste to recover the high excess lime present. The cake will pass to a multiple hearth furnace and be lightly calcined at a temperature in the range 500°-600°C (900°-1100°F). At this temperature the organics will be consumed supplying part of the fuel needed and the magnesium will be converted to an "active" form of MgO readily soluble in CO_2. The $CaCO_3$ will not be calcined at that temperature.

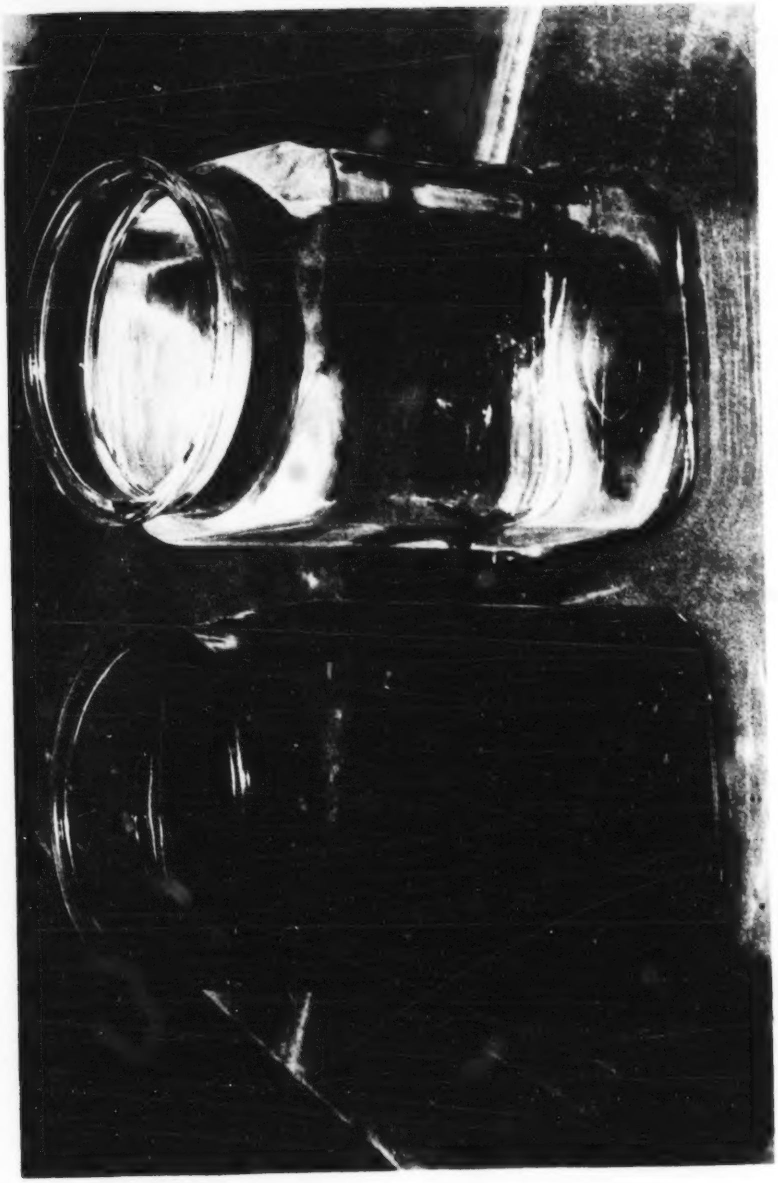
The calcined sludge, now a mixture of $CaCO_3$, MgO, metal phosphates, silicates and silica, will be slurried, carbonated as described and the carbonated liquor stored or recycled. It was not possible to obtain a vacuum filter and small multiple hearth furnace for the pilot plant. However, these operations were carried out on small batches of a few pounds using a laboratory muffle furnace for

FIGURE 2
VIEW OF PILOT PLANT









the calcination process. The calcined sludge was an odor free, gray to brown powder, with no hard lumps or pebbles and from which the magnesium could be easily recovered by carbonation.

To determine the percentage of magnesium which may be recovered by such a series of operations, a large laboratory sample of sludge was prepared by coagulating five drums of raw wastewater. The resulting sludge was collected on a vacuum filter and calcined in the laboratory muffle furnace at 550°C. The cooled calcined material, friable and light gray in appearance, was ground, suspended in distilled water and carbonated to pH 7.5, at which point this present work and the Dayton work have shown that all of the $Mg(OH)_2$ has been converted to the soluble bicarbonate. Analyses of the carbonated liquor showed 99% recovery. The amount of phosphate, if any, dissolved by the operation was not checked. Should it prove to be appreciable, it would be removed in the next pass of the recycling procedure and would not pass into the settled effluent from the primary clarifier.

An Expanded Concept of the Magnesium Process

As previously discussed, the preferred method of magnesium recovery is filtration of the thickened sludge and light calcination of the filter cake or, perhaps the thickened sludge itself without filtration. In either case, the calcined sludge would be composed mainly of calcium carbonate, together with an active and readily soluble form of magnesium oxide, metal phosphates (mainly $Ca_3(PO_4)_2$), silica and silicates. It would be slurried, carbonated with 20% CO_2 from the furnace to pH 7.5, settled or filtered and the clarified liquor containing magnesium bicarbonate recycled to the plant influent.

From this point, either of two courses could be followed and a third, the most attractive, should be carefully studied.

Course 1, the simplest—Convey the cake to landfill. This would eliminate lime recovery and recycling and substantially increase treatment costs.

Course 2, direct recalcination—This would result in the production of lime of poor quality, containing all phosphates and silicates. With the price of lime certain to increase substantially due to the energy crisis, this becomes somewhat more attractive.

Course 3, not yet proved possible—This would involve two steps. The first would be the separation, by selective flotation, of the $CaCO_3$ from the phosphates and silicates. If this can be done, a much higher quality lime could be produced by recalcining and recycling the high dosages needed. The rejects, namely phosphates and silicates with some $CaCO_3$, would be disposed of as landfill, as in Case 1, above.

The second also deserves careful study since it would completely eliminate all solid waste discharges from a physical-chemical waste treatment plant. It would involve:

> Removing NH_3 from the coagulated and filtered effluent with the naturally occurring ion-exchange mineral clinoptilolite. When the column is exhausted, acid stripping with H_2SO_4 to recover NH_3 as $(NH_4)_2SO_4$. This acid solution containing excess H_2SO_4, would then be used to acidulate the phosphate-silicate slurry of Course 3.
>
> Assuming a "normal" municipal waste containing 15 ppm nitrogen, equivalent to 18 ppm NH_3, and 9 ppm phosphorus, equivalent to 27 ppm PO_4, calculations indicate that the above process would theoretically yield for each million gallons of waste treated, about 1,200 lbs dry weight of a 10-12-0 fertilizer worth, at Florida current prices, about $50 per ton. Cost of the H_2SO_4 needed at $30 per ton would be about $10.
>
> Figure 3 is a flow sheet embodying the entire process, including reduction of BOD and COD to effluent standards using granular carbon filters.

The influent and effluent data shown on Figure 2 are derived from a typical bench scale run.

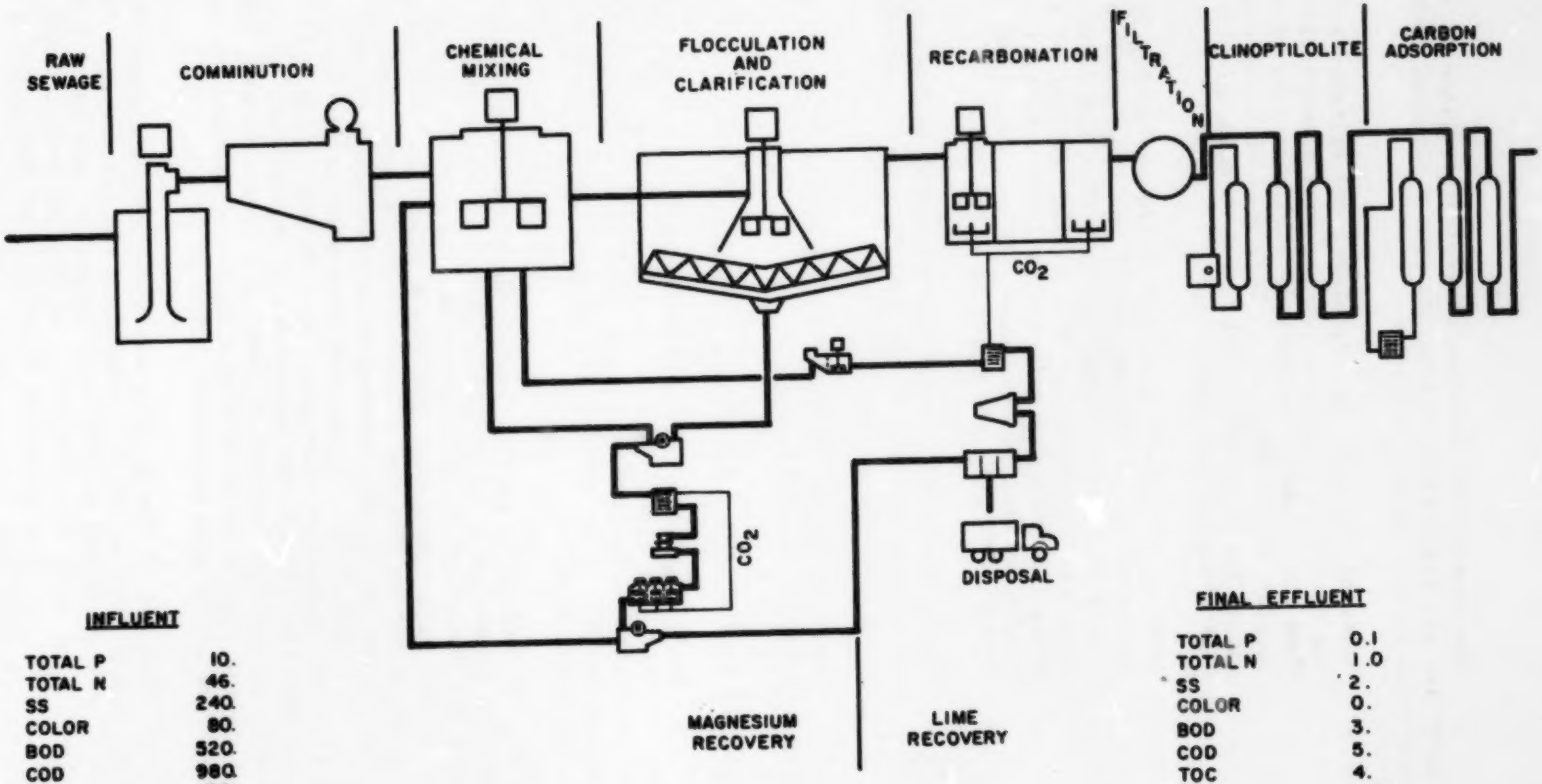
Study of Carbonation and Recovery of $MgCO_3 \cdot 3H_2O$

Since magnesium carbonate trihydrate is not now and never has been commercially available in this country, there is little information available concerning its physical and chemical properties. Information in the scientific literature is old and often conflicting in important details.

Accordingly, several pounds of very pure material was prepared from USP grade Epsom Salts, $MgSO_4 \cdot 6H_2O$ and caustic soda. The Epsom Salts was dissolved in distilled water and $Mg(OH)_2$ precipitated by adding the NaOH slowly with continuous stirring. The voluminous, snow-white precipitate was allowed to settle, the clear supernatant drawn off and the $Mg(OH)_2$ washed by decantation with distilled water until free from NaOH. It was then suspended in distilled water, cooled to 15°C and carbonated with pure CO_2. It was cooled only to 15°C since below that temperature the pentahydrate, $MgCO_3 \cdot 5H_2O$, is supposed to be formed. Since the carbonation reactinon is exothermic, the plastic carbonation drum is suspended in a slurry of cracked ice in a larger drum to maintain the temperature below 20°C.

When all of the $Mg(OH)_2$ was dissolved, the clear $Mg(HCO_3)_2$ liquor was warmed to 40°C by suspending the plastic drum in a larger drum of hot water and aerated with compressed air using a porous diffuser plug until the alkalinity of the hot solution had dropped to about 2,200 ppm, this being the solubility of $MgCO_3 \cdot 3H_2O$ at the temperature employed.

FIGURE 3
PROCESS FLOW SCHEME


RAW SEWAGE
COMMINUTION
CHEMICAL MIXING
FLOCCULATION AND CLARIFICATION
RECARBONATION
FILTRATION
CLINOPTILOLITE
CARBON ADSORPTION
CO2
CO2
DISPOSAL
MAGNESIUM RECOVERY
LIME RECOVERY

INFLUENT	
TOTAL P	10.
TOTAL N	46.
SS	240.
COLOR	80.
BOD	520.
COD	980.
TOC	138.
pH	7.5

FINAL EFFLUENT	
TOTAL P	0.1
TOTAL N	1.0
SS	2.
COLOR	0.
BOD	3.
COD	5.
TOC	4.
pH	9.5

The hot slurry was filtered on a large Buchner funnel, using No. 2 Whatman filter paper, washed with cold distilled water and pressurized as much as possible on the Buchner funnel. The filter cake was removed, chopped fine with a large spatula, spread out in a thin layer on cotton towels and allowed to air-dry for 24 hours in the air-conditioned laboratory. A 1 g/ℓ solution in CO_2-free distilled water will have an alkalinity as $CaCO_3$ of about 695 ppm and contains about 96% $MgCO_3 \cdot 3H_2O$ and 4% free moisture.

It is almost identical in composition with much older material, kept in closed containers, indicating that the material may be safely stored under water plant handling conditions.

Table 56 shows the results obtained by carbonating a batch of $Mg(OH)_2$ prepared as described above.

Table 56

Product Recovery by Carbonation of $Mg(OH)_2$

Time (min.)	Alkalinity P (mℓ)	Alkalinity T (mℓ)	$MgCO_3$ (mg/ℓ)	$Mg(HCO_3)_2$ (mg/ℓ)	Total (mg/ℓ)
0[a]	0.5	0.5	40	10	50
5[a]	2.9	6.9	580	110	690
10[a]	12.0	32.5	2,400	850	3,250
15	2.6	8.5	5,200	3,300	8,500
20	3.3	8.7	6,600	2,100	8,700
25	3.8	10.9	7,600	3,300	10,900
30	4.5	15.5	9,000	6,500	15,500
40	4.1	17.0	8,200	8,800	17,000
60	0	19.9	0[b]	19,900	19,900
80	0	24.3	0	24,300	24,300
90	0	25.6	0	25,600	25,600
100	0	26.2	0	26,200	26,200

[a] 0.02 N acid. All others 0.2 N acid.

[b] Increased CO_2.

Table 57 shows the rate of recovery of the $MgCO_3 \cdot 3H_2O$ by aerating the heated solution.

Table 57

Recovery of Product $MgCO_3 \cdot 3H_2O$

Time (min.)	Alkalinity as $CaCO_3$* P	T (mℓ)	M	$Mg(HCO_3)_2$	$MgCO_3$
0	0	26.2	26.2	26,200	0
5	1.8	25.6	24.8	22,000	3,600
15	1.5	13.5	12.0	10,500	3,000
30	0.4	8.3	7.9	7,500	800
45	0.4	5.5	5.1	4.700	800
60	0.4	4.3	3.9	3,500	800
75	0.4	3.6	3.2	2,800	800
90	0.4	2.9	2.5	2,100	820

Note: Initial temperature 42.5°C, final 36°C. Continued aeration would have converted all remaining $Mg(HCO_3)_2$ to $MgCO_3 \cdot 3H_2O$ but with little additional recovery.

*0.2 N acid.

Table 58 shows the data obtained by determining the alkalinity of product prepared above with other samples as described.

Recovery of Magnesium Bicarbonate Liquor from Gainesville Tap Water

In order to have the storage tank filled with magnesium bicarbonate liquor to be used as makeup in the first few cycles of waste treatment, it is necessary to employ some convenient source of magnesium. Gainesville unsoftened and softened municipal water represent possible sources. Since essentially selective softening is used, removing mainly calcium hardness, the softened water contains about 40 ppm of magnesium as calcium carbonate. There is no convenient source of raw water available to our pilot plant so that the softened water was used. The pilot plant was placed in operation, removing the magnesium as $Mg(OH)_2$ by excess lime treatment. The resulting sludge was carbonated and the carbonated liquor stored for later use. This "shake-down" during several days of operation provided an opportunity to check the calibration of all feed pumps and locate and correct any operational difficulties.

Table 58

Alkalinity as $CaCO_3$ of Selected Samples of $MgCO_3 \cdot 3H_2O$

Sample No.	Alkalinity as $CaCO_3$ mℓ H_2SO_4	Alk.	% $MgCO_3 \cdot 3H_2O$	% H_2O
1	17.4	696	96.0	4.0
2	17.5	700	96.5	3.5
3	17.25	690	95.0	5.0
4	17.4	698	96.3	3.7
5	17.5	700	96.5	3.5

Note: Solutions contain exactly 1.0000 g $MgCO_3 \cdot 3H_2O$ per liter.

Description of Samples:

Sample 1:	Prepared by A. P. Black from Dayton sludge in August, 1969. Air-dried. Bottle 75% filled.
Sample 2:	Same as above and ground. Bottle 40% full.
Sample 3:	Another batch prepared by A. P. Black from Dayton sludge in late 1969. This sample "cottony." Bottle 10% filled.
Sample 4:	Material prepared by Black and Thompson from Dayton sludge early in 1971. Bottle 50% filled.
Sample 5:	Sample of material prepared by A. P. Black and Arley DuBose in August, 1972. Air-dried. Bottle 95% filled.

On November 7, 1972, the pilot plant was placed in operation using municipal tap water. This selectively softened water contains about 40 mg/ℓ of magnesium as calcium carbonate. This was precipitated by adding hydrated lime slurry, just as it will be when wastewater is being treated. The resulting floc was very thin and light as would be expected, since little or no $CaCO_3$ is formed using softened water. The large flocculator paddles and the speed of rotation destabilized the floc particles, preventing agglomeration. The four 9-foot paddles were removed and replaced with 2-foot paddles. The minimal speed of rotation (4 RPM) was known to be excessive, but provisions for further reducing this speed were not readily available. In order to build up the floc more readily, Epsom Salts (magnesium sulfate) was fed into the tap water prior to the addition of lime. The shorter paddles and additional magnesium sulfate improved the floc size and settling characteristics.

The first batch of settled sludge was drawn into the carbonation tank on November 9. This sludge (66 gallons) was carbonated and the results appear in Table 59. The carbon dioxide used was determined by weight difference in the cylinder. A set of scales has been loaned to the project from the water plant for this operation.

Table 59

Carbonation of Sludge

pH	Time (min.)	CO_2 (lbs)	Alkalinity		
			OH	CO_3 (mg/ℓ)	HCO_3
12.2	0	0	338	76	--
10.4	10	1		696	304
9.9	20	2		1,520	720
9.5	30	4		1,440	2,000
8.6	40	6		480	4,880
7.9	50	8		0	5,280

The supernatant liquor containing the $Mg(HCO_3)_2$ was removed from the carbonation tank into a 55-gallon drum. Thirty pounds of $MgSO_4$ was then added to this solution prior to feeding it back to the tap water.

A second batch of sludge was drawn into the carbonation tank and allowed to settle overnight. Additional settling did take place and the supernatant was discarded. This same process was repeated twice in order to build a more concentrated sludge slurry. The resulting thickened sludge amounted to 175 gallons and the carbonation run is shown in Table 60.

An additional source of magnesium was provided by Dixie Lime and Stone Company of Ocala, Florida, in the form of dolomitic ground limestone. The magnesium concentration was 30% by analysis. The limestone was mixed with the hydrated lime and fed to the tap water. The hydrated lime utilized during this period was the dolomitic variety which contributed an additional increment of magnesium. Carbonation of the resulting sludge (Table 61) produced a stronger magnesium stock solution.

After running the pilot plant 6 hours per day for three weeks, a thick sludge had developed that was difficult to stir using the

Table 60

Carbonation of Thickened Sludge

pH	Time (min.)	CO_3 (lbs)	Alkalinity OH	Alkalinity CO_3 (mg/ℓ)	Alkalinity HCO_3
12.2	0	0	456	56	0
10.4	20	2		288	72
9.8	30	4		800	200
9.7	40	6		1,600	400
9.0	50	10		1,200	3,400
8.6	60	12		1,000	5,000
7.6	80			0	7,600

Table 61

Carbonation of Sludge
November 27, 1972

pH	Time (min.)	CO_3 (lbs)	Alkalinity CO_3 (mg/ℓ)	Alkalinity HCO_3 (mg/ℓ)
9.2	30	5	2,000	1,800
8.3	60	10	1,600	6,000
7.8	90	15	--	10,400

available equipment. Since dilution of the sludge with tap water would elute an even greater quantity of magnesium and provide for more efficient mixing, a 2 to 1 mixture of sludge and tap water was carbonated (Table 62).

Operation of Pilot Plant Using Raw Sewage

On December 6, 1972, raw sewage was started through the pilot plant at 25 gpm. The plant was run 6 hours per day for one week.

Table 62

Carbonation of Sludge
November 28, 1972

pH	Time (min.)	CO_3 (lbs)	Alkalinity CO_3 (mg/ℓ)	Alkalinity HCO_3 (mg/ℓ)
9.3	30	5	2,400	1,600
8.6	60	10	4,000	4,400
7.8	90	15	--	8,600
7.5	120	20	--	13,500

The floc was thick and settled well. The pH was easily maintained between 11.4 and 11.6. The only difficulty encountered was the breaking up of the floc by the overflow weir in the flocculation tank. Some settling of floc particles took place in the flocculation tank. The overflow weir will no longer be utilized. Two 8 in. pipes were installed below the overflow trough to carry the solids directly to the settling basins. In addition, two side-mounted mixing plates have been removed from the flocculator tank. Carbonation of the sewage sludge is shown in Table 63. No odor was present in this sludge.

Table 63

Carbonation of Sewage Sludge
(66 gal. tap water, 40 gal. sludge)

pH	Time (min.)	CO_3 (lbs)	Alkalinity OH (mg/ℓ)	Alkalinity CO_3 (mg/ℓ)	Alkalinity HCO_3 (mg/ℓ)
12.0	0	0	520	80	0
9.6	30	3		1,200	1,800
8.4	60	5		3,200	4,000
7.8	90	8		0	10,700
7.3	120	10		0	12,000

Pilot Plant Additions and Improvements

1. In order to evaluate the benefit of return sludge, a 2 in. pipe was installed to transport the settled sludge back to the rapid mix tank. Operation of the plant using returned sludge did not visibly improve the clarity of the supernatant. In addition, the use of the rapid mix was shown to produce a smaller floc due to excessive mixing speed. Thus, the rapid mix is no longer utilized.

2. A previously installed baffle in the settling basin was positioned at an angle to the inlet pipes (2"—8") from the flocculator producing excessive velocities in the settling basin. This baffle (4' × 8') was moved two feet back into the settling basin and installed on a true vertical to within 5 feet of the bottom. Operation of the plant under this condition produced a marked improvement in the settling of the floc and clarity of the supernatant.

3. Two flowmeters were installed for more accurate measurement of the CO_2 gas being utilized. The high rate flowmeter (20 lbs/hr) is used in the recarbonation of the settled sludge, while the smaller flowmeter (7.5 lbs/hr) is used on the recarbonation basin for pH adjustment.

4. In order to operate the pilot plant continuously for more than 24 hours an additional magnesium bicarbonate tank was constructed and installed.

5. A wash water storage tank for backwashing the dual media filter was constructed and installed. This tank is for holding high pH (11.5) wash water. Provision has also been made for washing the filter with tap water and the normal operating procedure uses only tap water for backwashing the filter.

6. A second 70 gpm submersible pump has been installed in the comminutor. Thus, a spare pump is ready in case of pump malfunction during extended runs.

7. During construction of the pilot plant no provision was made for draining or wasting sludge from the settling basin. The rapid buildup of sludge in the settling basin required this action and a drain line was installed.

Alternate Methods for Operating the Reactor-Clarifier

The 2,500-gallon cylindrical tank, which is equipped with a vertically mounted paddle flocculator, has been operated as a combined mixing and flocculating reactor. It has been found that liquid turbulence created by the paddles at only 2 rpm is sufficient for complete reaction and the subsequent growth of large floc particles. Doubling the paddle speed to 4 rpm was found to destabilize the flocs and the unit was rebuilt to provide the slower paddle rate.

The fluidized sludge bed is allowed to rise to the level of two 8 in. lateral transfer pipes which permits the sludge to flow by gravity and with minimum turbulence to the sludge settling basins. It has been impossible to prevent some breaking up of the large floc particles and the resulting fines pass from the sludge settling basins to the larger combined settling and carbonation basin. It has been found that the use of activated silica as a flocculant aid provides a stronger floc with less fines.

An alternate and probable preferable way to operate the unit would be to hold the level of the fluidized sludge bed below the level of the two 8 in. effluent pipes and allow the clear almost turbidity-free clarified liquor to pass directly to the settling-carbonation basin. This is usual practice in up-flow solids-contact reactors of water plants. However, in waste treatment plants the surface of the clarified liquor is covered with a film of grease and entrapped solid matter such that an effluent weir cannot be used. It would be necessary to maintain the levels in the tank such that the two 8 in. effluent pipes are above the sludge level but below the dirty surface and this cannot be done in practice on a continuous basis.

For this work, a flocculant will not be used to toughen floc particles. Actually, the passage of a small amount of destabilized floc would not normally be of concern, but in a wastewater treatment plant it should be held to a minimum since it contains a certain amount of the finely divided amorphous calcium phosphate which is redissolved in the carbonation step which follows.

Extended Pilot Plant Operation on Weak Wastewaters

During the period April 11, 1973 to April 13, 1973, a 48-hour run was conducted. The results are presented in Table 64. No carbonation was carried out prior to filtration by the dual media filter. Average chemical dosages were:

$MgCO_3 \cdot 3H_2O$ (present in sewage and added)	90 mg/ℓ
$Ca(OH)_2$ (90%)	435 mg/ℓ

A composite of the two-hour samples was analyzed for BOD. The influent was 132 mg/ℓ and the effluent 16 mg/ℓ.

Table 64

48-Hour Pilot Plant Run

		Influent			Effluent		
Date	Time	COD	TOC	Total P	COD	TOC	Total P
		mg/ℓ					
4-11-73	12 M.	336	96	9.5	58	34	0.42
	2 P.M.	302		12.6	61		0.33
	4 P.M.	398	113	23.4	62	34	0.22
	6 P.M.	291		10.2	64		0.56
	8 P.M.	312	85	13.4	70	37	0.83
	10 P.M.	325		12.0	65		0.29
	12 P.M.	224	59	12.4	55	28	0.34
4-12-73	2 A.M.	112		9.4	44		0.21
	4 A.M.	78	54	8.4	36	19	0.25
	6 A.M.	67		7.9	36		0.18
	8 A.M.	220	60	9.0	28	17	0.58
	10 A.M.	329		6.4	24		0.24
	12 M.	336	95	11.2	37	22	0.34
	6 P.M.	370			62		
	12 P.M.	213			50		
4-13-73	6 A.M.	67			36		
	12 M.	434			34		

Note: Four-hour lag time (4 P.M. influent is 8 P.M. effluent).

The values from each of the two-hour samples were averaged and the results shown below:

	Influent	Effluent
pH	7.1	11.5
Alkalinity	116 mg/ℓ	215 mg/ℓ
COD	260 mg/ℓ (total)	48 mg/ℓ (filtered)
Total P	11.2 mg/ℓ	0.37 mg/ℓ
TOC	81 mg/ℓ	27 mg/ℓ

An influent flow of 50 gpm was maintained for the entire period. Approximately 4 gal./ft^2/min passed through the dual media filter.

During the period April 17, 1973, to April 20, 1973, a 72-hour run was conducted. Chemical dosages were the same as the prior week. However, carbonation was employed prior to dual media filtration. The phosphate content in the effluent increased due to the redissolving of fine floc by CO_2.

The filter run the first week was 40 hours, while the second week a 60-hour run was observed. Table 65 presents the analytical data collected.

The values from each of the three-hour samples were averaged and the results shown below:

	Influent	Effluent
pH	7.1	10.0
Alkalinity	123 mg/ℓ	145 mg/ℓ
COD	347 mg/ℓ (total)	56 mg/ℓ (filtered)
Total P	6.7 mg/ℓ	0.48 mg/ℓ
TOC	86 mg/ℓ	32 mg/ℓ

A composite of the three-hour samples was analyzed for BOD. The influent was 180 mg/ℓ and the effluent 30 mg/ℓ.

Table 65

72-Hour Pilot Plant Run

Date	Time	Influent COD	Influent TOC	Influent Total P	Effluent COD	Effluent TOC	Effluent Total P
		mg/ℓ					
4-17-73	3 P.M.	472	123	7.6	61	42	0.68
	6 P.M.	493	126	7.9	62	39	0.45
	9 P.M.	448	90	7.8	61	39	0.43
	12 P.M.	469	60	5.7	63	39	0.47
4-18-73	3 A.M.	134	41	2.8	50	37	0.27
	6 A.M.	78	25	2.1	49	25	0.40
	9 A.M.	540	132	8.4	54	23	0.66
	12 M.	505	96	8.8	63	17	0.36
	3 P.M.	450	113	9.1	65	42	0.85
	6 P.M.	495	131	8.2	81	36	0.76
	9 P.M.	405	101	7.7	72	36	0.54
	12 P.M.	225	64	5.8	56	34	0.36
4-19-73	3 A.M.	89	37	2.8	53	33	0.70
	6 A.M.	56	18	1.9	40	20	0.38
	9 A.M.	378	95	8.9	43	23	0.20
	12 M.	473	158	9.4	27	22	0.18
	3 P.M.	562	124	8.4	56	37	0.58
	6 P.M.	402	106	9.2	62	38	0.62
	9 P.M.	403	101	7.8	65	39	0.81
	12 P.M.	302	74	5.7	62	35	0.57
4-20-73	3 A.M.	134	40	3.1	63	37	0.40
	6 A.M.	112	30	2.8	45	23	0.33
	9 A.M.	549	85	7.7	36	21	0.25

Comparison of Pilot Plant Run and Table 27

Table 27 represents a close approximation to the raw sewage encountered during the period of April 17, 1973 to April 20, 1973. Comparison of the average COD, TOC, and BOD values for the pilot plant run to this table shows quite favorable agreement. The raw BOD of the table was 136 mg/ℓ and the pilot plant was 180 mg/ℓ. The filtered BOD of Table 27 was 19 mg/ℓ and the pilot plant was 30 mg/ℓ. The TOC of the pilot plant (raw) was 86 mg/ℓ and Table 27 was 132 mg/ℓ. The filtered effluents were the same. The COD of the raw sewage for the pilot plant was 347 mg/ℓ and Table 27 was 387 mg/ℓ. The filtered effluents were the same.

The only significant difference between Table 27 and the pilot plant was that carbonation was performed on the pilot plant run and not in Table 27.

Comparison of Pilot Plant Runs and Table 28

Table 28 compares other physical-chemical processes to the earliest jar tests of this research. Comparison of this table to the pilot plant runs (average values) shows some improvement using the magnesium carbonate process.

For example, comparison of the work of Hannah (Table 28) to the pilot plant run of April 8, 1973 shows:

		COD	BOD	TOC
		mg/ℓ		
Hannah	Before	265	139	78
	After	66	28	23
Gainesville Pilot Plant 4-8-73 Run	Before	260	132	81
	After	48	16	27

Comparing the work of Bishop (Table 28) to the pilot plant run of April 15, 1973, shows:

		COD	BOD	TOC
		mg/ℓ		
Bishop	Before	347	142	118
	After	66	31	26
Gainesville Pilot Plant 4-15-73 Run	Before	347	180	86
	After	56	30	32

The detailed analyses of the two-hour samples of the April 11, 1973 to April 17, 1973, pilot plant run are shown on Table 64. Table 65 displays the analyses of the three-hour samples collected from April 17, 1973 to April 20, 1973. Comparison of these hourly samples with Table 28 may be made by including a four-hour time lag between the influent and effluent for the week of April 11 and a three-hour time lag for the week of April 17.

Extended Pilot Plant Operation on Medium Strength Wastewaters

Table 66 displays a summary of five weekly runs. Each run was conducted under increasing magnesium precipitated conditions. The data shown are averages from Tables 67, 68, 69, 70, and 71. Figure 4 shows typical COD curves.

The municipal wastewater of Gainesville averages 40 mg/ℓ magnesium (as $CaCO_3$). Therefore, a baseline for lime only treatment had to be determined at the highest pH which would not precipitate any magnesium ion (pH 11.1). The 5 mg/ℓ magnesium precipitated run required only a slight addition of lime to bring down half of the magnesium occurring naturally in the sewage. The 10 mg/ℓ magnesium precipitated run required adding makeup magnesium since approximately 12 mg/ℓ magnesium (as $CaCO_3$) cannot be precipitated from the sewage but remains complexed.

The data show increased improvement in the effluent characteristics even though the raw sewage increased in strength over the test period. Shock loads from 200 mg/ℓ to 1,000 mg/ℓ COD were encountered each week. The process responded by showing a lower residual in the effluent COD each week as the magnesium was increased. Phosphate removal increased from 1.3 mg/ℓ residual for lime only to 0.1 mg/ℓ for 30 mg/ℓ magnesium ion precipitated.

The length of filter runs showed an increase from 30 hours for lime only treatment to 72 hours for 30 mg/ℓ magnesium ion precipitated.

Bacteriological samples were collected during the weeks of June 5, 1973, and June 26, 1973. The membrane filter technique was used to determine total coliforms per 100 mls. Grab samples were collected from the raw sewage entering the pilot plant at the flow control box. The effluent from the dual media filter served as the other collection point. Counts for the raw sewage averaged 4 million per 100 mls. The filter effluent (pH 9.5) showed 0 to 20 coliforms per 100 mls.

FIGURE 4

TYPICAL COD REDUCTION CURVES

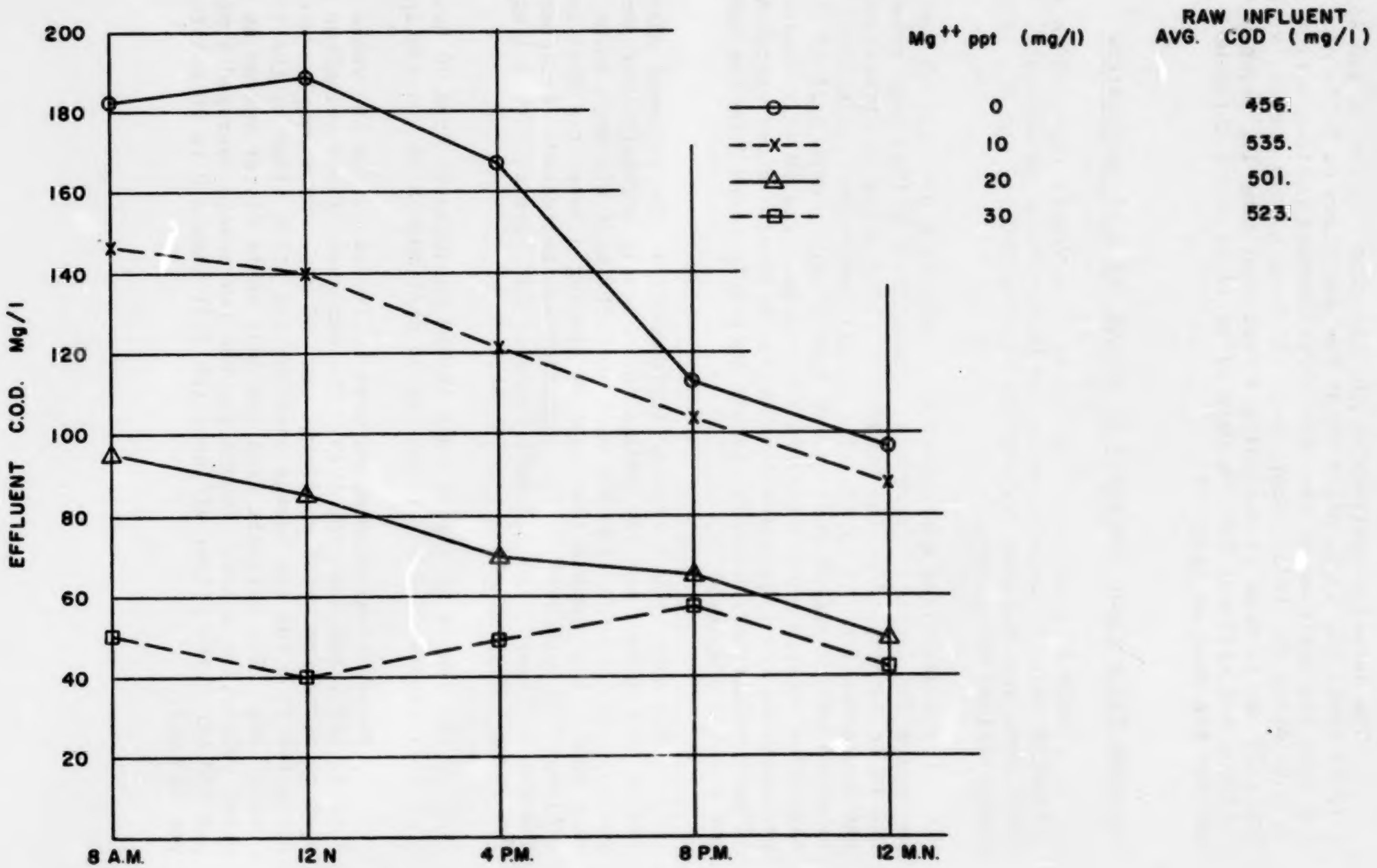


Table 66

Effect of Increased Magnesium Precipitated

Date	Mg^{++} ppt	Lime Added	COD		BOD		TOC		Total P		pH
			In	Out	In	Out	In	Out	In	Out	
	mg/ℓ										
5-9-73	0	350	501	116	210	76	134	37	8.2	1.31	11.1
5-15-73	5	375	529	114	225	63	104	35	8.5	0.70	11.3
6-5-73	10	418	552	91	246	52	117	25	9.4	0.50	11.5
6-26-73	20	510	554	73	248	35	82	28	8.0	0.21	11.5
8-13-73	30	570	593	62	360	32	145	27	8.2	0.13	11.5

Table 67

Lime Only Treatment

		Influent			Effluent		
Date	Time	COD	TOC	Total P	COD	TOC	Total P
		mg/ℓ					
5-9-73	12 M.	603	181	8.9	184	59	2.40
	4 P.M.	423	127	9.2	187	51	2.18
	8 P.M.	342	79	7.0	166	46	1.84
5-10-73	12 P.M.	117	31	3.3	112	32	1.00
	12 M.	738	150	11.6	76	24	0.48
	4 P.M.	540	141	12.2	112	26	0.93
	8 P.M.	459	158	8.6	151	43	1.35
	12 P.M.	333	78	7.1	133	31	1.82
5-11-73	4 A.M.	153	50	3.1	83	34	1.42
	8 A.M.	225	48	5.3	61	29	1.26
	12 M.	1,116	275	12.0	97	29	1.12
	4 P.M.	612	164	9.5	72	46	1.42
	8 P.M.	1,656	533	8.7	162	52	1.68
	12 P.M.	396	50	7.1	137	45	1.15
5-12-73	4 A.M.	126	40	3.6	122	42	1.11
	8 A.M.	252	60	10.2	72	26	0.62
	12 M.	423	110	12.0	47	20	0.42

Note: Four-hour time lag (4 P.M. influent is 8 P.M. effluent).

Table 68

5 mg/ℓ Magnesium Precipitated

		Influent			Effluent		
Date	Time	COD	TOC	Total P	COD	TOC	Total P
		----------------------	----------------------	--------------mg/ℓ	----------------------	----------------------	----------------------
5-15-73	4 P.M.	513	110	9.6	139	34	0.82
	8 P.M.	707	118	8.4	147	42	0.64
	12 P.M.	571	94	6.6	132	36	0.64
5-16-73	4 A.M.	174	30	3.3	112	33	0.54
	8 A.M.	223	47	4.4	70	20	0.43
	12 M.	803	158	12.0	74	21	0.51
	4 P.M.	542	174	12.0	128	37	0.83
	8 P.M.	522	117	9.1	147	52	1.07
	12 P.M.	552	90	7.6	143	45	0.69
5-17-73	4 A.M.	174	28	3.1	116	32	0.61
	8 A.M.	281	52	4.5	70	21	0.48
	12 M.	736	124	11.8	115	36	0.91
	4 P.M.	620	163	9.5	155	50	1.20
	8 P.M.	842	109	9.1	163	50	0.91
	12 P.M.	474	87	8.0	139	35	0.67
5-18-73	4 A.M.	300	25	3.2	108	26	0.52
	8 A.M.	846	125	10.3	12	6	0.05
	12 M.	649	112	12.0	77	19	0.52

Note: Four-hour time lag (4 P.M. influent is 8 P.M. effluent).

Table 69

10 mg/ℓ Magnesium Precipitated

		Influent			Effluent		
Date	Time	COD	TOC	Total P	COD	TOC	Total P
		mg/ℓ					
6-5-73	12 M.	553	118	10.7	146	29	0.46
	4 P.M.	669	142	9.3	140	40	0.71
	8 P.M.	535	119	9.2	120	38	0.57
6-6-73	8 A.M.	295	59	7.5	89	18	0.46
	12 M.	821	130	11.0	71	18	0.54
	4 P.M.	803	160	9.8	96	25	0.53
	8 P.M.	749	127	8.6	136	39	0.51
6-7-73	8 A.M.	312	109	4.4	53	16	0.44
	12 M.	491	113	11.2	46	20	0.28
	4 P.M.	455	98	9.4	86	27	0.55
	8 P.M.	500	93	9.1	103	14	0.57
6-8-73	8 A.M.	437	113	10.0	57	20	0.41
	12 M.	517	146	12.0	68	27	0.50

Note: Four-hour time lag (4 P.M. influent is 8 P.M. effluent).

Table 70

20 mg/ℓ Magnesium Precipitated

		Influent			Effluent		
Date	Time	COD	TOC	Total P	COD	TOC	Total P
		mg/ℓ					
6-26-73	4 P.M.	434	89	8.0	--	--	--
	8 P.M.	399	79	6.7	77	29	0.23
	12 P.M.	--	--	--	74	--	0.21
6-27-73	8 A.M.	1,215	83	4.4	70	[illegible]	--
	12 M.	434	96	10.6	94	21	0.15
	4 P.M.	417	97	8.7	87	33	0.17
	8 P.M.	651	109	6.8	72	34	0.26
	12 P.M.	--	--	--	66	33	0.22
6-28-73	8 A.M.	495	55	9.5	50	--	--
	12 M.	469	76	7.9	80	23	0.18
	4 P.M.	477	52	9.3	56	25	0.24
	12 P.M.	--	--	--	--	26	0.23

Note: Four-hour time lag (4 P.M. influent is 8 P.M. effluent).

Table 71

30 mg/ℓ Magnesium Precipitated

Date	Time	Influent COD	Influent TOC	Influent Total P	Effluent COD	Effluent TOC	Effluent Total P
		mg/ℓ					
8-13-73	4 P.M.	482	173	8.8	40	--	--
	8 P.M.	580	107	6.8	55	--	.10
8-14-73	12 P.M.	500	95	6.3	46	20	.07
	12 M.	700	183	10.5	68	21	.10
8-15-73	12 M.	1,356	412	24.9	72	30	.14
	4 P.M.	819	116	5.7	97	31	.18
	8 P.M.	382	87	4.2	86	28	.16
8-16-73	8 A.M.	527	100	3.9	68	31	.15
	12 M.	482	108	5.4	56	26	.13
	4 P.M.	498	118	6.0	42	24	.12
	8 P.M.	591	96	--	58	32	.18

Note: Four-hour time lag (4 P.M. influent is 8 P.M. effluent).

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SECTION VIII. APPENDIX

The laboratory studies were conducted using one-liter samples. The dosages of magnesium carbonate trihydrate ($MgCO_3 \cdot 3H_2O$) and 98% calcium hydroxide ($Ca(OH_2)$) were weighed out on an analytical balance in 15 and 25 ml beakers, respectively. A portion of the one-liter wastewater sample was retained in a 200 ml beaker in order to prepare slurries of the chemicals and rinse the slurries from the beakers. A glass stirring rod with a rubber policeman was utilized to facilitate preparation of a uniform suspension. The magnesium slurry was quantitatively transferred to the rapidly stirred (70 rpms) sewage sample. The beaker is then rinsed with two successive portions of wastewater and the washings added to the jar. After three minutes the lime slurry was added and the rapid mix continued for an additional two minutes. The speed was then reduced to 35 rpms. After twenty minutes the stirrers were slowly removed prior to cutting off the jar test machine. The suspension was then allowed to settle for ten minutes prior to direct sampling or filtration.

Magnesium carbonate trihydrate, $MgCO_3 \cdot 3H_2O$, is a white powder of fine particle size and a bulk density of 40 lbs/cu ft. The air-dried product contains about 4% moisture and a dry basis is about 99.7% pure. This chemical should always be weighed out and added as a slurry. Water solutions of the material slowly decompose to form the relatively insoluble "basic" carbonate, $4\ MgCO_3 \cdot Mg(OH)_2 \cdot 3H_2O$.

"Magnesium carbonate" purchased from any source will be the basic carbonate, $4\ MgCO_3 \cdot Mg(OH)_2 \cdot 3H_2O$. The low solubility, 90 mg/ℓ, slowness to dissolve and extremely low bulk density, 5-8 lbs/cu ft, make it unsatisfactory for practical use. It should not be used for jar tests.